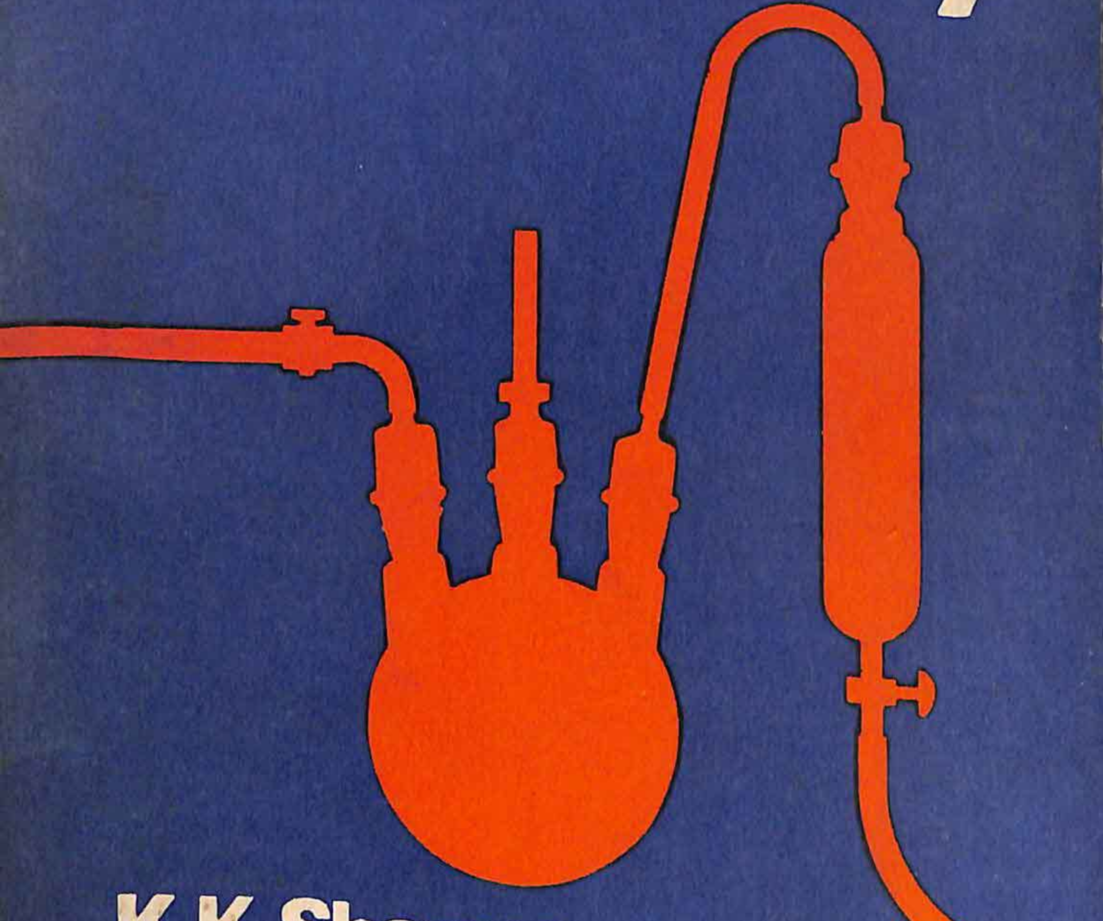
An Introduction to Practical Chemistry



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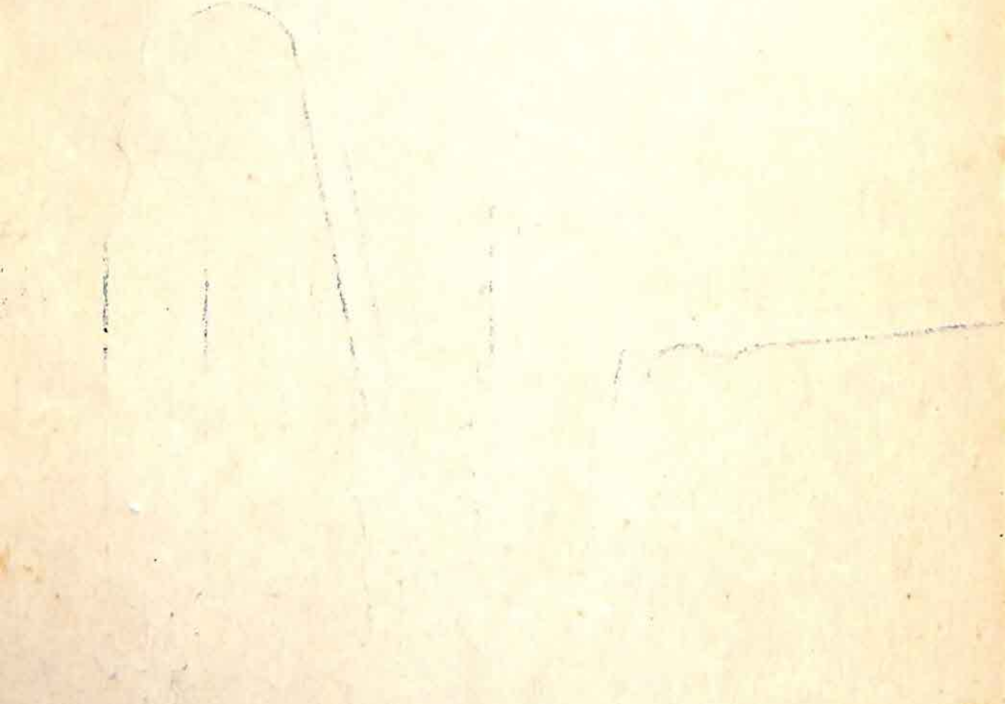

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PREFACE

It is gratifying to note that the first edition of this book has been very well received. The features of the book that it contains experiments in all the three branches of Chemistry, i.e., Inorganic, Organic and Physical Covering that syllabii of B.Sc. (Pass and Hons.), B.Sc. (Engg.) and B.Pharm. has been appreciated.).

In this edition the suggestions given by students and teachers of various Universities in India and abroad have been incorporated. The printing errors have been throughlly removed. At certain places the experimental techniques have been suitably modified. Further suggestions for the improvement of the book will be gratefully acknowledged.

AUTHORS

PREFACE TO THE FIRST EDITION

In writing this laboratory textbook we have been conscious of the profound changes that have taken place in the curriculum of chemistry at all levels. The combination of workable experiments with detailed experimental background and the operational information will enhance students' interest in the laboratory and enable them to perform effectively and with confidence.

A thorough description of the laboratory operations has been given so that students can begin their experiment after knowing what they are to observe and how to direct their experiment to a successful conclusion. We believe that the approach we are using is new in many respects and we envisage that the book will be of immense help to the students of chemistry.

The book contains three sections i.e., Inorganic Chemistry, Organic Chemistry and Physical Chemistry. General tools and techniques used in the laboratory are introduced at the beginning which should serve as good foundation. Inorganic Chemistry section contains the theoretical principles and the experimental details in volumetric analysis including complexometric titrations, gravimetric estimation and qualitative analysis of mixtures containing interfering and insolubles.

Organic Chemistry section contains detailed procedures for the systematic identification of monofunctional compound, chromatographic technique, detection of food adulterants, and laboratory scale preparations of some compounds of commercial significance.

Physical Chemistry section contains simple experiments on molecular weight determinations, solid state and transition temperature measurements, surface tension and viscosity of liquids, thermochemical measurements, simple experiments in colloids reaction kinetics, potentiometric and conductometric measurements. The chapter on Treatment of Experimental Data discusses some methods of treatment of experimental data.

In the preparation of this volume authors have utilised pertinent material wherever it was found. A comprehensive Appendix has been added which contains much useful information for the practising chemist.

The book will be suitable inter-alia for students preparing for

B.Sc. B.Sc. (Hons.), B.Sc. (Engg.) and B. Pharm. students of all universities.

In conclusion the authors wish to gratefully acknowledge the help from our colleague Dr Sulekh Chandra, lecturer in Chemistry, Zakir Husain College, and the Editorial Staff of Vikas Publishing House Pvt Ltd.

Any suggestions for improving the book will be gratefully received by the authors.

K.K. SHARMA
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GENERAL INSTRUCTIONS

A good scientist is, first of all, a careful observer. The purpose of laboratory work in chemistry is to train a student in the art, and, school him in the scientific principles, upon which the art is founded. The real understanding of the principles, which underlie all laboratory techniques and procedures, is possible only if a student plans his work carefully in advance, and works purposefully during each laboratory period. For a distinguished achievement and efficient performance in each experiment a student should work with an open and inquiring mind. The caliber of a student is oftenly adjudged by his technique. note-book report and his understanding of the practice and principles involved in the experiment as revealed by oral or written quizzes which his instructor gives him from time to time. Nothing will be more personally rewarding or gratifying to a student in the laboratory than the type of intelligent and skilled workmanship.

Preparation for Experiment

(*a*) **Before coming to the laboratory.** Above all, it is important that you study the experiment of the day carefully before coming to the laboratory. Master, in advance, the theoretical principles involved and list the equipment and chemicals in condensed form in your note-book. In order to finish the work within prescribed time, you must be familiar with the procedure and be ready to start at once. When possible write your outline of the procedure, tables for weighings and titration data and write the balanced equations for the reactions involved. Careful planning in advance will enable you to work fast and efficiently.

(*b*) **While in the laboratory.** Record all the observations and data in a logical manner. Record, not what you think is supposed to happen, but what you actually observe. Be aware of what you are doing at all times and why you are doing it. As you work, ask yourself questions, if after determined effort you cannot answer them, do not hesitate to ask your teacher.

(*c*) **Handling reagents.** Reagents should be located in a systematic manner so that they may be readily available. Reagent bottles should be returned to their place on the reagent shelf immediately after use and should not be left on the desk in haphazard fashion. While using the reagents, the stopper should never be placed on the working table, hold the stopper between the fingers. Reagent bottles should be kept stoppered except when they are in use. Do not pour any reagent directly from a bottle into strongly acidic or basic solutions or into hot solutions. While pouring liquids from bottles, one should pour on the side opposite the label, so that the label is not spoiled. Do not leave any reagent bottle without a label on it.

(*d*) **Amount of Reagent to be used.** In semi-micro analysis, one should not use more than 3-4 drops of the solution under investigation. A slight excess of the reagent (1-6 drops) is sufficient to obtain a complete reaction. In precipitation reactions also a slight excess of reagent is frequently used; however, a large excess of reagent sometimes produces undesirable effects. In case the reagent is solid then it should be added with the help of small spetula or small spoon which can measure 50 to 100 mg of the substance.

(*e*) **Laboratory note-book.** Careful observance of the plan of your laboratory work is the very essence of meaningful experimentation. All the observations should be properly recorded in the permanently bound note-book. The pages should be numbered and the first two pages reserved for an index. Enter all data and observations into the note-book, whether or not they will be used. Do not tear the leaves or erase anything. If any thing is not wanted it should be crossed with an explanatory note. Never use scrap paper for your observations as this can be lost or confiscated. Enter data in a reasonably neat manner and have them initialed by an instructor before leaving the lab. A report format is given below:

Outline Reporting a Laboratory Experiment?

Left hand page	*Right hand page*
Observations Give all weighings and titration figures in full. Many experimental forms are best recorded in the form of tables. *Calculations* Give the complete calculations along with subtitles so that it is easily	*Experiment No.* Date . . . . Title. *Theory* *Reactions.* Give molecular and ionic reactions. *Procedure* Outline briefly the working method in impersonal statements.

---

followed.

Result

Give the result with units, if any.

Correct Value

Percentage error

Precautions

Record the Precautions.

Note: The format is not rigid and may be changed slightly according to the experimental requirements. However, a neat logical and easily followed format is generally acceptable.

(*f*) **Safety**. All too often chemical laboratories are the scene of accidents—mostly minor ones but some of serious nature. These are caused by carelessness and improper procedures. The following precautions, if they are observed sincerely, would definitely prevent most such mishaps. A student by cultivating these habits of safety can perform his experiments smoothly and can avert the possibility of accidents in the laboratory.

(1) *Safety-glasses and lab-coat*. The eyes are particularly vulnerable to injury by splashing droplets of chemicals or flying particles of glass. Wearing protective spectacles in the laboratory at all times, particularly during potentially dangerous operations, is an excellent safety measure. One should never try to look into the open mouth of a test tube or flask in which a reaction is being conducted.

To protect your clothing from soiling and damage by chemicals and accidents, you are strongly urged to wear an inexpensive laboratory coat.

(2) *Eye accidents*. Flood your eyes immediately with water. For an acid, use dilute sodium bicorbonate solution; for an alkali, use dilute boric acid solution.

(3) *Burns—Acids*. Wash immediately with large quantities of water, then with dilute (8%) sodium bicarbonate solution. If burn is severe, wash again with water and apply the acriflavine.

Alkali. Wash immediately with water and 1% acetic acid solution.

Bromine. Wash immediately with ample supply of petrol, when the bromine will be completely removed from the skin.

Organic substances. Wash immediately with soap and warm water.

(4) *Cuts*. Wash the wound with sterile gauze, soap and water. Disinfect with an antiseptic and apply a bandage.

(5) *Reagents in mouth*. If the reagent is in the mouth and not swallowed then spit out at once, and wash the mouth out repeatedly with water.

If swallowed. If the substance is acid or alkali, dilute by drinking much water. Then for acids follow by drinking much lime-water. Milk may be given but no emetics. For salts of heavy metals give milk or white of egg. For arsenic or mercury compounds, give emetic without any delay.

(6) *Fire hazards*. When using inflammable solvents, do not light matches or burners and do not keep excess solvent in open beakers. Waste solvents must be discarded into the container provided. Never pour them into the sink. Familiarize yourself with location of the fire extinguisher.

(7) *Gas poisoning*. Remove patient to fresh air and loosen clothing at neck. If breathing has stopped, give artificial respiration until the doctor arrives.

To counteract bromine or chlorine fumes if inhaled in only small amounts, inhale ammonia vapour, or gargle with sodium bicarbonate solution. Afterwards suck eucalyptus pstilles, or drink warm dilute pippermint or cinnamon essence to soothe the throat and lungs.

(8) *Shun explosive mixtures*. Strong oxidizing agents and easily oxidized material must be mixed with extreme caution and in small amounts. Never add HNO_3 to a flask containing alcohol or other easily oxidised material. The reaction between nitric acid and organic reducing agents can be so violent that a dangerous explosion may result.

GENERAL PRECAUTIONS

1. Never work in the laboratory unless a demonstrator or teaching assistant is present. A minor mishap that may be of little consequence if someone is at hand to help you, may be serious if you are alone.
2. Do not throw waste such as match stems, filter papers etc. into the sink. They must be thrown into the waste jars.
3. Keep the water and gas taps closed except when these utilities are needed.
4. While working with obnoxious gases, conduct the experiment in a fume hood.
5. Do not swing glass-ware in a circular arc to dry it. Such spattering of your neighbours is inexcusable.
6. Sodium metal should be used with extra care and scraps of sodium should never be thrown into the sinks. Sodium should

be kept covered with kerosene.

7. Keep all the doors and windows open while 'working in the laboratory
8. Bromine, acetyl chloride, benzoyl chloride, phosphorous trichloride etc. are obnoxious materials and they should be carefully handled in the hood.

1

General Tools and Techniques

Introduction

Quantitative analysis is concerned with the determination of the amount of a chemical substance present either alone or in a simple or complex mixture of other substances. Unlike qualitative analysis, there is no general scheme of experimental techniques that find general use after being determined. Quantitative analytical methods may be broadly divided into two general groups. Group I consists of those methods in which the final measurement of the substance sought is made by direct or indirect measurements of volume and weight after proper treatment of a measured portion of the material to be analysed. This group covers the two most important methods:

(*i*) Gravimetric method.

(*ii*) Volumetric or Titrimetric method.

Group II consists of those methods in which the final measurement is made upon the system as a whole. Almost any physical measurement may be used in this group to give the desired analytical result.

Further, in quantitative analysis a distinction is made between macro-, micro-, and semi-micro methods.

In macro analysis relatively large samples (about 0.1g or more) of solids or large volumes (tens of millilitre or more) of solutions are taken. In micro and semi-micro methods samples weighing between 1mg and 50mg and solution volumes between tenths of a millilitre and several millilitre are used. The main advantages of the micro and semi-micro methods are their high speed and the need for only very small amounts of material. Despite these advantages the classical macro method, which is the oldest and the most convenient method of quantitative analysis, is the one most widely used at the present time Only the methods of quantitative macro analysis are considered in this book. This chapter deals with the tools and techniques employed in these methods, whereas the next two chapters give the detailed study.

1.1. THE ANALYTICAL BALANCE

The balance is the principal instrument used in quantitative analysis. The analytical results obtained by any method must be referred to a

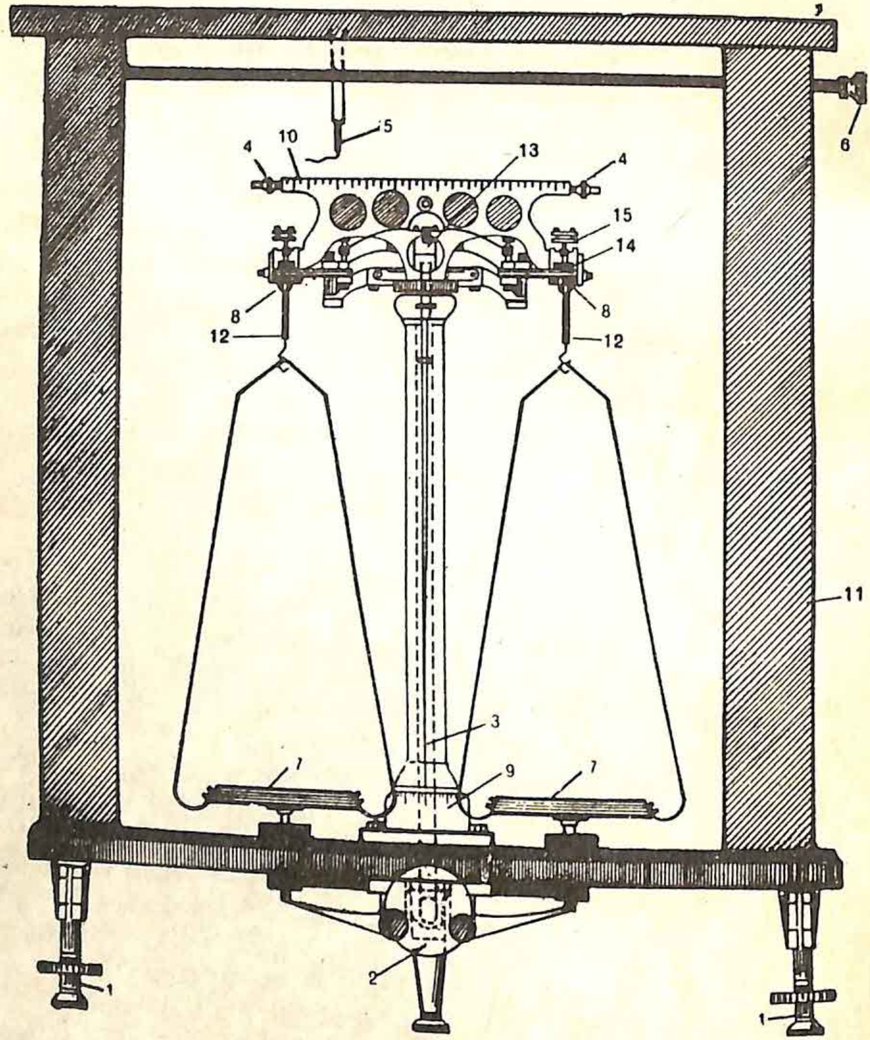


FIG. 1.1

definite quantity of the given substance; for example, as a percentage of its weight. Therefore, the first stage in analysis is usually to weigh out a definite sample of the substance for investigation. The accuracy of the analysis may be limited by the accuracy of the weighing involved. An analytical balance, therefore, must be accurate and is normally required to weigh to one ten-thousandth of a gram, 0.0001g. The analytical balance is used in quantitative analysis. Macro analysis can be used for weighing objects not heavier than 100-200mg, i.e., 0.2g.

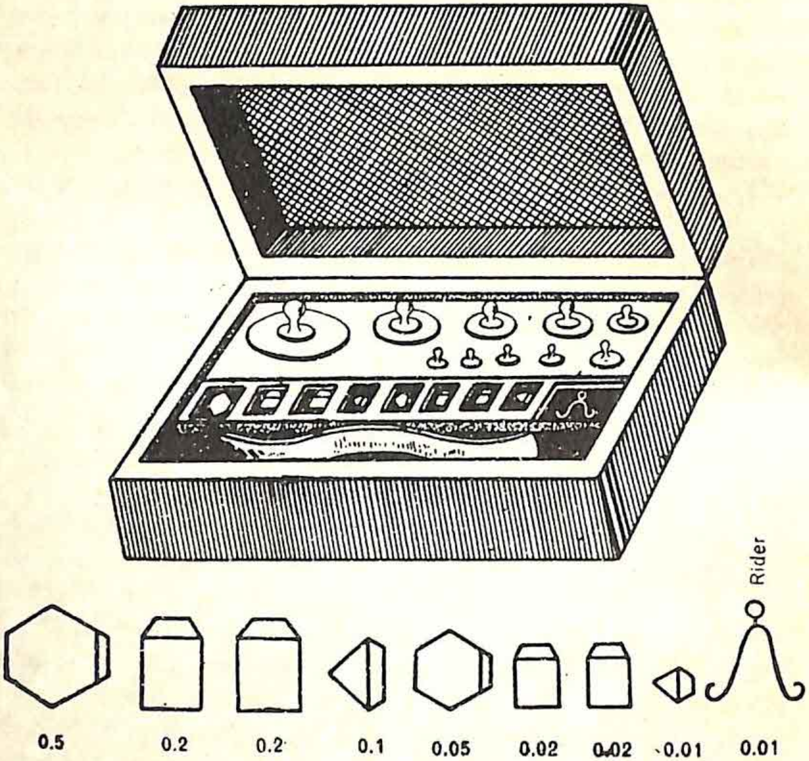
The most usual design of a balance of this type is shown in Fig. 1.1.

The two-pan balance consists essentially of a beam (10), with a central knife-edge, and two pan knife-edges (8), set at the ends of the beam. All three knife-edges are pressed permanently into the beam, with the central one pointing downward and the end ones pointing upward. The central knife-edge rests on an agate plate (13), set on the post, (15). The pan knife-edges bear on agate plates (14), which are set in stirrups (12), which in turn support the pans (7). Each stirrup ends in a double hook; the upper holds the pan and the lower is for the suspension of objects that cannot be set securely upon the pan.

On the lower front of the platform on which the case rests is a milled knob (1). When this knob is turned it lifts the beam off the knife-edges and loosely hung stirrups are held firmly in place. A push-button (2), which is concentric with the beam arrest knob (1), activates the pan arrests and lightly supports the pans to prevent them from moving when the beam is lowered on the knife-edges. If the beam is lowered on the knife-edges and the pan arrests released, the beam and the pans will move in the manner of a compound pendulum. The movement is observed by means of a pointer (3), which swings over the scale (9). The small brass collar, *K*, is movable along the pointer, and is used to adjust the sensitivity of the balance. The whole assembly is covered by a protective glass case (11), to keep out drafts, dust and corrosive fumes. A rider hook attached to the rider rod permits the rider (5) to be placed on any scale division. This is adjusted from the outside of the case with the rider control (6).

1.2. WEIGHTS

The weights used with analytical balances are contained in a special box (Fig. 1.2) which also contains a pair of foreceps for lifting the weights and putting them on and off the balance pans The foreceps should be ivory-tipped. There are nine integral weights: 100g, 50g, 20g, 10g, 10g, 5g, 2g, 2g, and 1g. There are also eight or more fractional weights. These are 500mg, 200mg, 100mg, 100mg, 50mg, 20mg, 20mg, and 10mg. Sometimes 5mg, 2mg and 1mg weights are also included but these weights i.e., less than 10mg should never be used as weights from 0.10mg to 10mg. are added by placing the rider at different positions on the graduated beam.



Box and weights

FIG. 1.2

The beam is usually graduated into 10mg numbered divisions on each side of the fulcrum. If the rider is placed on the tenth division it balances its own weight, 0.01g on the opposite pan. If the rider is placed on the first division then, by the lever principles it balances one-tenth of its own weight or 0.001g, on the second it balances

0.002g, on the fifth 0.005g, etc. It follows that each division on the beam corresponds to 0.001g or 1mg.

The space between two consecutive numbered divisions is further divided into five equal parts. Each of these parts obviously corresponds to 0.0002g (0.2mg). If, for example, the balance is in equilibrium when the rider is in the position shown in Fig. 1.3, then the reading on the beam corresponds to 0.0056g. This is added to the weights on the scale pan.

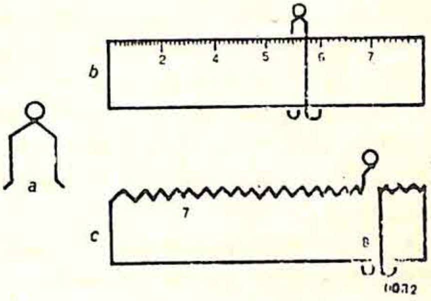


FIG. 1.3

General Rules for Use of the Balance. (*i*) The beam support and pan arrests must be raised and lowered gently to avoid damage to the agate knife-edges.

(*ii*) Weigh chemicals in weighing bottle. Remove spilled chemicals immediately with a soft brush.

(*iii*) Never put a wet or hot objects on the pan. A hot object would set up convection currents within the balance and it is possible that a hot object could cause distortion of metal parts of the balance.

(*iv*) The weights must never be touched by hand.

(*v*) Be sure that the beam arrest is secured before putting an object on the pan. Release the beam gently. The beam is swinging on knife-edges that must be kept in perfect condition.

(*vi*) Never overload a balance. For most analytical balances, the maximum capacity is 200g on each pan.

(*vii*) Close the balance case completely before making a final weighing. This excludes drafts from outside, causing the pan to swing excessively.

(*viii*) Always record the weight immediately and to four decimal places.

(*ix*) In any weighing operation always check the individual values and the summation of the values of the recorded weights. Errors in reading weights are easily made.

(*x*) After weighing, leave the balance clean and the balance door closed.

1.3. WEIGHING A SOLID SAMPLE

Two general methods are employed for weighing a solid sample.

(*a*) **Direct weighing.** This is preferred method when exactly specified quantity is required. Small quantities of substance can be added or removed until the exact weight is reached. When a large quantity of the substance is to be weighed, it becomes more convenient. For direct weighing, a clean vessel or weighing paper is weighed first. The substance added is then transferred without loss to another vessel. The quantity of substance contained in the vessel or on the paper is thus known.

The disadvantages are that the weight of the container plus sample is limited by the capacity of the balance. Further, this method is more time consuming.

(*b*) **Weighing by difference.** In weighing by difference, the substance is taken in a weighing bottle which is weighed. Handle the weighing bottle with a paper loop and not with your fingers, because moisture and grease from the fingers will change the weight. Remove carefully an estimated amount of sample from the weighing bottle and place in a marked beaker or flask. Weigh the remaining sample along with the bottle to the nearest 0.01g to determine whether the amount of sample withdrawn is within the desired weight range. If necessary remove more sample and reweigh the bottle until sufficient sample has been transferred. Now weigh the bottle plus the remaining sample accurately. The weight of sample transferred is obtained by subtracting the final weight from the initial weight.

This method is generally preferred for weighing a series of samples. To illustrate, if fine samples are to be weighed, this method would require six weighings whereas ten weighings are required by direct-weighing method. This method must be used for a hygroscopic compound or one unstable to air, because the weighing bottle is closed except when the substance is bejng removed.

Weighing a liquid sample. If a liquid is non-corrosive and relatively non-volatile, it can be weighed by transferring it into a weighed container with a tight-fitting cover or stopper, such as weighing bottle of liquid can be weighed, some liquid transferred to another container using the dropper, and the bottle reweighed to determine the amount of liquid transferred.

Note. If the rider is placed on the left hand side of the beam, the weight has to be subtracted.

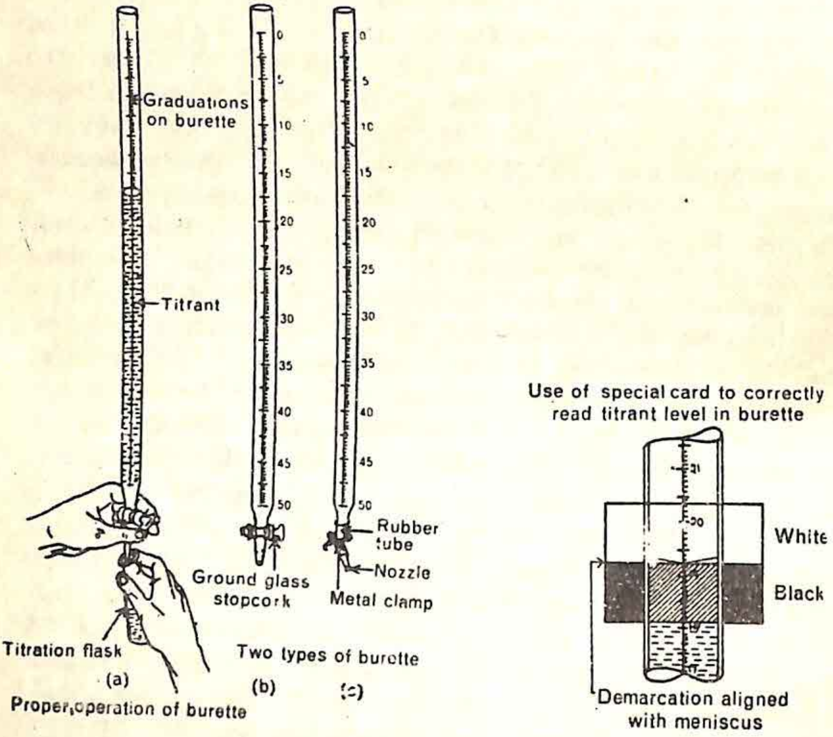
1.4. TOOLS AND TECHNIQUES OF VOLUMETRIC ANALYSIS

The fundamental unit of volume is the litre, which is the volume of one kilogram of water at the temperature of maximum density (3.98) and one atmospheric pressure. One thousandth part of a litre is called a millilitre and is used where the litre is inconveniently large. The cubic centimetre (c.c.) is another volume unit. Although this and the millilitre (ml) can be used interchangeably, these units are not strictly identical. One millilitre is equal to 1.000028 cubic centimetre. In volumetric analysis, the litre and millilitre are frequently used.

To provide reliable and accurate measurement of volume three types of apparatus are indispensable to the performance of a volumetric analysis. They are burette, pipette and volumetric-flask. These can be calibrated either to deliver or to contain a specific volume. The mark 'TD' on volumetric equipment indicates 'to deliver', whereas TC stands for 'to contain' at a specified temperature. The temperature of 20°C is chosen as the standard temperature for calibration as the laboratory temperature is normally very close to this. For ordinary analytical work temperature corrections are not required. Soda-lime glass is used satisfactorily for the construction of volumetric ware. Ordinarily solutions are not allowed to remain in them for a long period of time, hence contamination by chemical attack of the glass is not serious. Volumetric flasks and burettes of pyrex may be obtained, if required for resistance to chemical attack. Resistance to thermal shock is not of much importance in volumetric ware, which should not be heated much above room temperature because it returns to volume equilibrium very slowly.

(*a*) **Burette.** The burette is used for titration and consists of a cylindrical calibrated tube with a constricted end to which a narrow glass tube is attached by means of rubber tubing. On the free part of the rubber tube there is a spring clip. If the rubber is pressed gently over the glass ball, narrow channels are formed between the rubber and the ball, and the liquid can flow out of the burette. The burette is graduated in millilitres and tenths of millilitres the zero being at the top. A burette is shown in Fig. 1.4. (*a*) and (*b*).

Volumes are measured by filling the burette with liquid to the upper part of the graduations, reading the level of the liquid, and then reading the level again after the liquid has run out through the stopcock. It is better to use a burette reader. A common type of reader is in the form of a card made of opaque plastic material. The upper half of the card is white and lower half is black. While reading the burette, the dividing line is adjusted at the same



(a) Proper operation of burette

Two types of burette (b) (c)

Use of special card to correctly read titrant level in burette (d)

FIG. 1.4

level, see Fig. 1.4(d). Parallax is avoided by adjusting the position of the burette to the eyes so that the front and rear of the coloured liquids, such as potassium permanganate the top of the level of liquid is read. Before use, the burette must be perfectly clean. This can be done by treating the inside of the burette with a warm solution of chromic acid in concentrated sulphuric acid. Before each titration, the liquid level in the burette must always be adjusted to the zero mark, i.e., the same part of the burette must be used each time. In this way the graduation errors in the burette can be compensated. For accurate titration results, the volume of solution used in a titration should not exceed the volume of the burette, but at the same time it should not be too small.

(*b*) **Pipette.** A pipette usually consists of a narrow tube in the middle of which is a bulb with a capacity little less than that indicated on the pipette. The upper narrow part of pipette has a line up to which it must be filled. Pipette is used to transfer known volumes of liquid from one container to another. Some deliver a single fixed volume, these are called volumetric or transfer pipettes others known as measuring pipettes are calibrated in convenient units so that any volume up to the maximum capacity can be delivered. Typical pipettes are shown in Fig. 1.5. The transfer-pipettes require a complete drainage. This can be done by placing the tip of the pipette against the inside of the vessel to which the solution is to be transferred. The sample is allowed to drain freely. After waiting for 20 seconds for drainage, the tip of the pipette is allowed to touch the wall of the vessel and the pipette is rotated a few times and removed, the small quantity of liquid inside the tip is not to be blown out.

Transfer pipette (left) and graduated pipette (right)

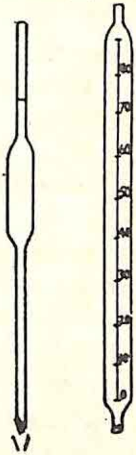


FIG. 1.5

(*c*) **Volumetric flasks.** Volumetric flasks have a flat bottom, pear-shaped body and a long narrow neck. These are usually calibrated to contain the specified volume when filled to the line etched on the neck, and are used in the preparation of standard solutions and is the dilution of sample to known volumes before taking aliquot positions with

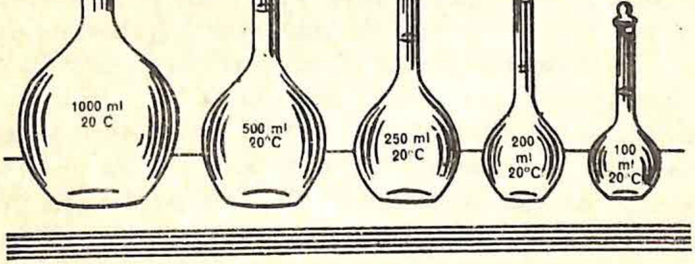


FIG. 1.6

a pipette. The flasks most commonly used have capacities of 25, 50, 100, 250, 500 and 1000ml as shown in Fig. 1.6.

1.5. CALIBRATION OF VOLUMETRIC APPARATUS

When using apparatus of good quality it may not be desired for beginners to attempt calibration of such apparatus. The reasons for this being, firstly, the operations are time consuming. Secondly, with inexperience in analytical technique the calibrated apparatus may be less accurate than the apparatus calibrated by the manufacturer. Thirdly, the assumed tolerances are usually less than the expected error permitted in a determination by a beginner. If calibration seems desirable, the procedures are outlined below.

(*a*) **Calibration of a burette.** Clean the burette thoroughly and lubricate the stop-cock properly. Fill the burette with distilled water and note the room temperature. Run the water for convenient intervals, i.e., 5 or 10ml into weighing bottle and weigh accurately to the nearest one-hundredth of a gram. The readings should be estimated to the nearest hundredth of a millilitre. Tabulate all observations. Now actual volume delivered for each interval is obtained by multiplying the weight of this volume by the volume occupied by one gram of water at the room temperature (Table 1.1) On any interval, duplicate calibrations should agree within 0.03ml.

(*b*) **Calibration of a pipette.** Clean the pipette thoroughly and fill it with distilled water from a beaker of water containing a thermometer, so that the temperature of the water is known. Deliver the contents of the pipette into the weighed flask, and weigh again. Find by difference the weight of water delivered, and then find the volume of the pipette, using Table 1.1. Repeat the calibration of the pipette. The average of the two determinations should be used as the calibration correction for the pipette.

(*c*) **Calibration of the volumetric flask.** Flasks may be calibrated in a similar manner to that described for burettes and pipettes. However, their larger volume requires the use of the oversized balance. Calibration correction may be determined by using Table 1.1.

Relative calibration of the volumetric flask and pipette. If many analysis are performed in which aliquots of a single sample are titrated, it is desirable to calibrate the volumetric flask and pipette relative to each other, so that an aliquot pipetful is taken it will amount to a simple, integral fraction of the sample, thus simplifying computations.

TABLE 1.1

Weight of water to give true litre at 20°C at 760 mm.

Temperature °C	*Wt. of true litre in air, g*	*Volume occupied by 1g-ml*	*Temperature* °C	*Wt. of true litre in air, g*	*Volume occupied by 1g-ml*
10	998.39	1.0016	21	997.00	1.0030
11	998.32	1.0017	22	996.80	1.0032
12	998.23	1.0018	23	996.59	1.0034
13	998.14	1.00186	24	996.38	1.0036
14	998.04	1.0019	25	996.16	1.00385
15	997.93	1.0021	26	995.93	1.0041
16	997.80	1.0022	27	995.69	1.0043
17	997.66	1.0023	28	995.44	1.0046
18	997.51	1.0025	29	995.18	1.0048
19	997.35	1.0026	30	994.91	1.0051
20	997.18	1.0028			

The calibration procedure is as follows: Prepare a clean 50ml pipette and a clean, dry 250ml volumetric-flask, fill the pipette to the mark and empty it five times in succession into the flask. If the level does not correspond with the mark on the neck of the flask, paste a label with its upper edge on a level with the bottom of the meniscus. The volume of the flask now bears a direct relationship to the volume of the pipette.

For the usual analytical quality volumetric apparatus, limits of error, designated as tolerance, are given in the table below:

Apparatus	*Capacity, ml.*	*Tolerance, ±ml.*
Burette	25	0.06
	50	0.10
Pipette	5	0.02
	10	0.04
	25	0.06
	50	0.10
Flask	250	0.24
	500	0.30
	1000	0.60

1.6. TOOLS AND TECHNIQUES OF GRAVIMETRIC ANALYSIS

Preparation of crucibles. Crucibles used in the ignition process may be either porcelain or platinum crucibles must maintain a substantially constant weight throughout the drying of the precipitate. It is thus necessary to start with this constant weight condition. In general, the crucible or other vessel that is to be used in the final weighing is heated initially to constant weight at the same temperature and in the same manner that will be used later. Crucibles, other than platinum, weigh roughly 1mg less if brought to constant weight by heating at 700-800°C, than if brought to apparently constant weight at 100-110°C. A clean and absolutely dry crucible is put in a porcelain triangle resting on a tripod (Fig 1.7) and heated in the burner flame so that the blue cone

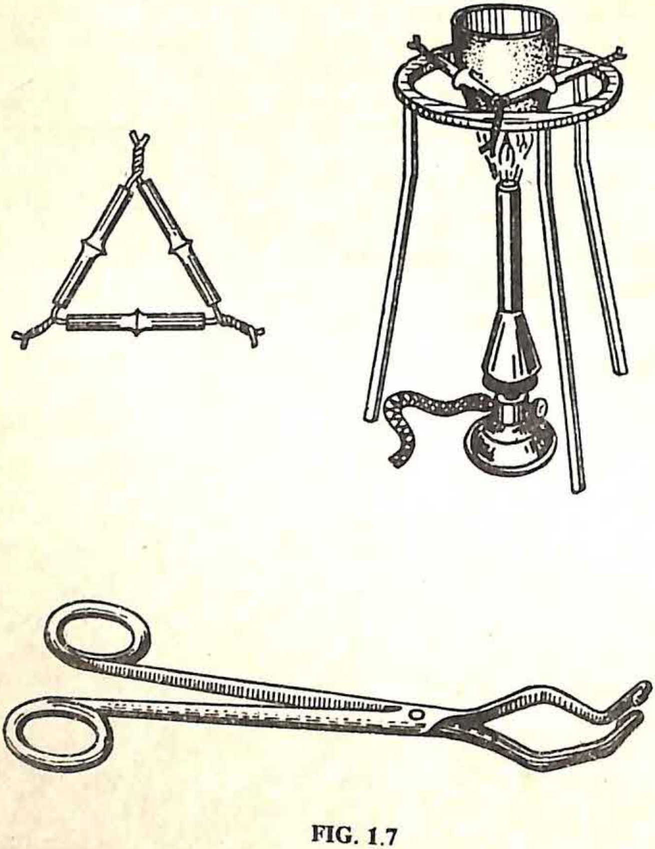


FIG. 1.7

of the flame is a few millimeters below the bottom of the crucible. After 15-20 minutes the burner is turned out, the hot crucible is allowed to cool in air for 1-2 minutes and then put into a desiccator for final cooling so that the crucible does not absorb moisture from the air and so increase in weight.

The crucible, after cooling down to the temperature of the balance, is weighed, the weight is noted down and the crucible is then heated again, cooled in the desiccator and weighed. Crucible should always be lifted by means of crucible tongs. If the second weighing does not differ from the first by more than 0.0002g, it may be assumed that the weight is now constant. Otherwise the heating and weighing is repeated as necessary.

(*a*) **Filter crucibles.** The most convenient way to filter a gravimetric precipitate is by suction through a crucible. The uses and properties of several types are described in the following sections:

(*i*) *Sintered-glass crucible.* A sintered-glass crucible is made of glass and has a bottom consisting of a porous disc made of glass particles which have been fused together so that the pores are of a uniform size. The nature of the precipitate determines which grade of porosity to use. Thus, Pyrex crucibles are made in three grades, coarse (C), medium (M), and fine (F). The crucible is very useful for heating precipitates below 500°C, at which temperature the glass begins to soften. Heating or cooling must be gradual, or the filter mat may crack.

(*ii*) *Gooch-crucible.* A Gooch crucible is made of porcelain and the bottom has holes in it approximately 0.1cm in diameter. A filtering pad must be placed over the holes to collect the precipitate. This pad can be filter paper cut to size, a glass-filter filter paper, or a compact mat of asbestos fibers, using the same mat over again, by filtering a second precipitate which has already been weighed from a previous determination is not recommended. Although, more troublesome to use than sintered-glass crucible, it is still less troublesome than filter paper. The

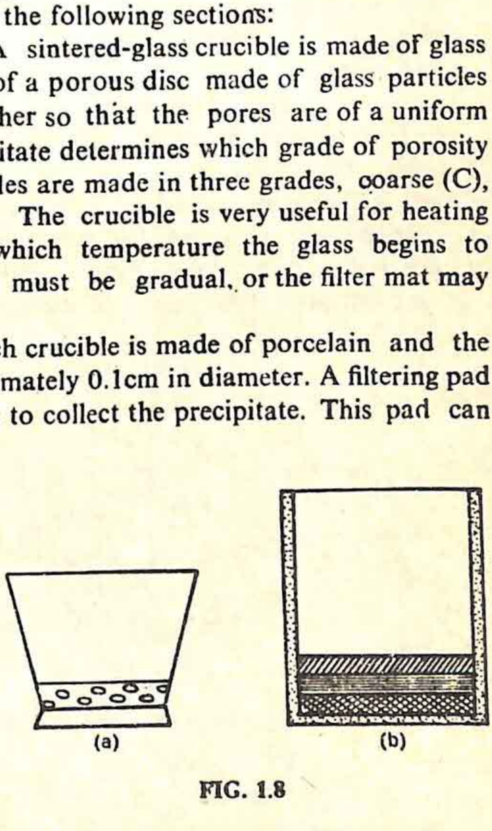

(a) (b)

FIG. 1.8

advantage over sintered-glass crucible is that it may be used for precipitates that must be ignited at high temperatures. Further, it may also be used to filter many solutions that react with paper, i.e., conc. HCl, permanganate, etc. or for precipitates that can not be ignited with paper.

The crucible should be washed thoroughly and should be inspected for defects. Prepare whichever filtering pad is asked for and dry for one hour at 110°C. Cool, and weigh, then repeat the heating and weighing until consecutive weighings agree within 0.2mg. The crucible can then be considered as being at constant weight.

(b) **Desiccator.** The desiccator is a large glass vessel provided with a tightly fitting cover in which the atmosphere is kept free from water vapour by a drying agent which is placed in the lower compartment. The purpose of a desiccator is to maintain an already dried object indefinitely in a dry condition. The ground glass rim of the desiccator and that of its cover are coated with a thin film of petroleum jelly or a special grease. This is done to make the vessel airtight granular or fused calcium chloride is drying agent (desiccant) used in the desiccator. The desiccator lid is always opened with a sliding motion and it should be opened as infrequently as possible.

It has been observed that hot objects cool slowly in a desiccator. If the desiccator is used to store an object while cooling prior to weighing, adequate time must be allowed. Some desiccators are equipped

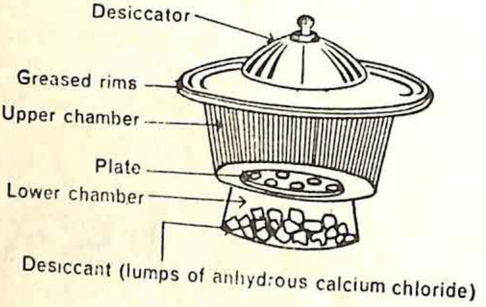


FIG. 1.9

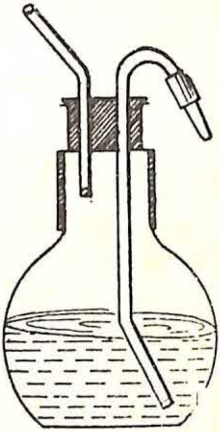


FIG. 1.10

with stopcocks, so that the air may be pumped out immediately after the objest is introduced. Moist materials should never be put in a desiccator but should be oven or air-dried first.

(c) **Wash-bottle.** A wash-bottle is a necessary piece of equipment. It is used for delivering a fine stream of distilled water or any other liquid for use in the transfer and washing of precipitates. It consists of a flat-bottomed flask of pyrex-glass having 500-1000ml capacity (*see* Fig. 1.10). The mouth tube is bent smoothly at an angle of 135° and the delivery tube at an angle of 45°. The delivery tube should extend nearly to the bottom and should be bent slightly at its lower end. The dimensions of the mouth tube and delivery tube should be such that they should lie in the same straight line. A gently tapered nozzle of about 5cm length is connected to the delivery tube with a piece of rubber tubing. The orifice of the jet should be approximately 0.5mm in diameter so that it will deliver a fine stream of liquid. Wash-bottles of polyethylene are now available (see Fig 1.11) The flexible unbreakable plastic gives easy control of a stream of wash liquid by simply squeezing the bottle.

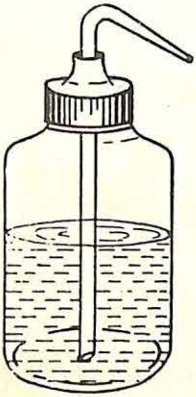


FIG. 1.11

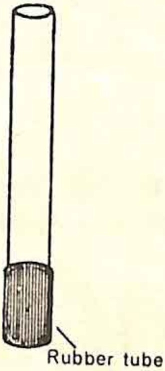


FIG 1.12

(d) **Rubber-policeman.** Removal of the last traces of precipitate is accomplished with a rubber policeman. This is a glass rod fitted at one end with a rubber tube closed at one end and flattened. This flexible tip allows the walls of the beaker to be scrubbed free of particles.

(e) **Filtering-assembly.** Filteration by a glass funnel and filter paper is usually a slow process. In certain operations filtration may be speeded up by the use of suction. This is most commonly carried out with some type of filtering funnel or crucible which is fitted to a special holder. The completed assembly is shown in Fig. 1.13.

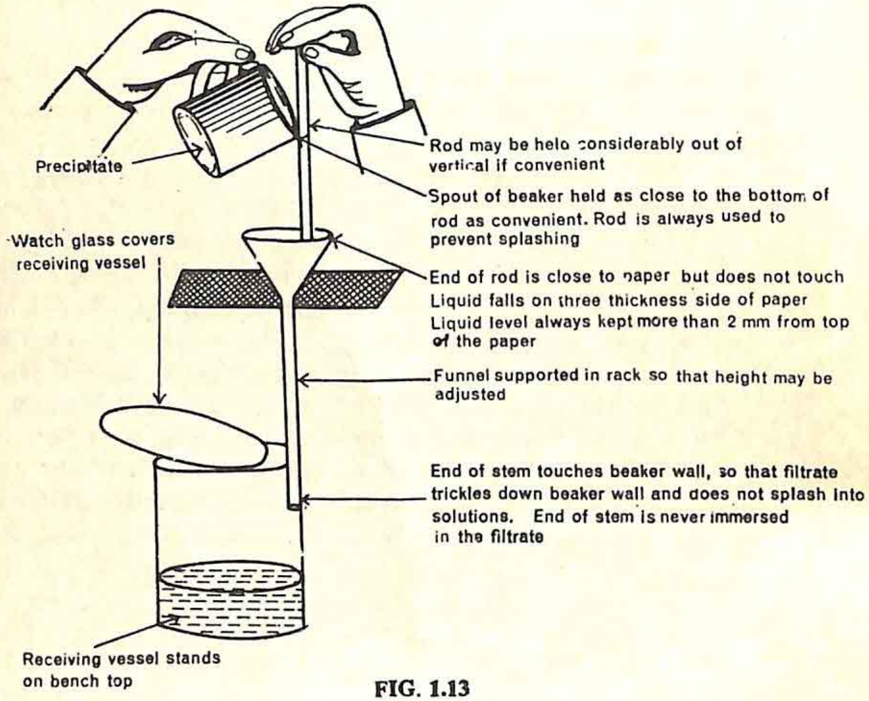
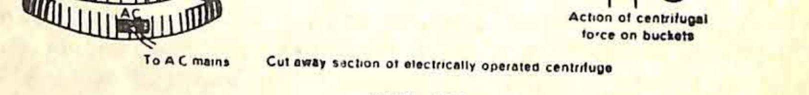

Precipitate
Rod may be held considerably out of vertical if convenient
Spout of beaker held as close to the bottom of rod as convenient. Rod is always used to prevent splashing
Watch glass covers receiving vessel
End of rod is close to paper but does not touch
Liquid falls on three thickness side of paper
Liquid level always kept more than 2 mm from top of the paper
Funnel supported in rack so that height may be adjusted
End of stem touches beaker wall, so that filtrate trickles down beaker wall and does not splash into solutions. End of stem is never immersed in the filtrate
Receiving vessel stands on bench top

FIG. 1.13

(*f*) **Centrifuge.** This is employed for separating precipitate from the solution. A typical centrifuge is shown in Fig. 1.14.



Cut away section of electrically operated centrifuge

FIG. 1.14

1.7. CLEANING OF GLASSWARE

The method of cleaning depends upon the type nature of impurity to be removed. Water soluble substances are simply washed out with cold or hot water. Ferric oxide, manganese dioxide, i.e., oxides in general are easily removed by hot conc. HCl. A greasy layer may be removed by acetone or by allowing a warm solution of 2% sodium hydroxide to stand in the vessel for several minutes, the vessel is then rinsed with water, hydrochloric acid and finally again with water. Many of the detergents, commonly found in any local market, are also effective cleansing agents.

When the glass ware fails to respond to the above cleaning operations, it should be washed with cleaning-solution, i.e., chromic-sulphuric acid mixture. Cleaning-solution is prepared by adding concentrated sulphuric acid to potassium dichromate and allowing it to stand for some time before use. Glassware to be cleaned is brought in contact with the mixture and allowed to stand for a period of 10-15 minutes. After standing the mixture is thoroughly drained off and the glass ware is washed with water repeatedly. The same cleaning solution can be used for a number of times till the colour of the mixture turns green. The dark green colour of cleaning solution is the indication of its ineffectiveness. The general use of cleaning solution is not recommended because of the destructive action of this mixture upon clothing, books, skin and laboratory furniture.

2

Volumetric Analysis

General Principles of Volumetric Analysis

In volumetric analysis the substance to be determined in the solution form is made to react with the measured volume of a solution of known concentration. Therefore, it is necessary to establish exactly the end point of the reaction. The reaction must satisfy a number of conditions and, therefore the applicability of the volumetric analysis is very much limited than that of gravimetric method. The advantage of volumetric method is its greater speed which is very important in practice, as for example in the chemical control of production. In order to be suitable for application of volumetric method a process must satisfy number of requirements.

(*a*) There should be only one single reaction occurring between the desired constituent and the titrant, so that calculations can be based upon the chemical change which occurs. There should be no side reaction.

(*b*) The reaction must be complete when equivalent amounts of reactants have been brought together. Only on this basis we can make the calculations from volumetric data.

(*c*) The reaction must be well defined. It means that it should proceed according to definite weight relations between reactants to form a definite product under given conditions.

(*d*) The reaction must be rapid, so that little time is lost in performing the titration.

(*e*) A suitable standard solution must be available as the titrant for carrying out the reaction.

(*f*) There must be a suitable indicator to mark the end point of the titration.

A solution of accurately known concentration is known as *standard solution*. It may be prepared either directly or by standardisation by reaction with a primary standard. A primary standard must meet certain requirements i.e., (*i*) It must be either 100 per cent pure or of a known purity. The impurities if present must be inert with respect to the substances with which it is brought into reaction. (*ii*) It should be stable at the oven temperature used for drying. The hydrated substances are seldom used as primary standard. (*iii*) The standard should be unaltered by contact with air during weighing, i.e., it must not be hygroscopic, nor it should react with oxygen or carbon dioxide at room temperature. (*iv*) A primary standard should be readily available, perferably at a reasonable cost. It should be perferably of high equivalent weight.

2.1. METHODS FOR THE EXPRESSION OF CONCENTRATION

In an aqueous solution, the weight of the solute in a given quantity of water is known as the concentration. The concentration of an aqueous solution is expressed by two methods.

(*i*) The weight of the solute dissolved in a given volume of solution, (*ii*) the weight of solute dissolved in a given weight of water or solution.

Weight of solute in a given volume of solution. The weight of solute in a given volume of solvent can be expressed in three ways, i.e., formality, molarity and normality.

Formality. It expresses the number of gram molecular formula weight of solute dissolved in sufficent water to produce a litre of solution. The formula weight is the sum of atomic weights of the elements appearing in accepted chemical formula of the solute, and this weight expressed in grams is the gram formula weight. For example, the formula weight of Na_2CO_3 is $(2 \times 23) + 12.0 + 3 \times 16.00$ or 106.00. The mass of one gram formula weight of Na_2CO_3 is 106.00. A 0.1F solution of Na_2CO_3 is prepared by dissolving 10.6 grams in sufficient water to produce one litre of solution. This method of expressing concentration has the advantage that no information about the properties of the substance in solution is required.

Molarity. It expresses the number of moles of a solute dissolved in sufficient water to produce one litre of the solution. The molecular weight is the sum of atomic weights of the elemants indicated in the formula of the substance, this weight expressed in grams is the gram-molecular weight.

The molar concentration and the formal concentration of a given solution are usually not the same. For example a solution of oxalic acid prepared by dissolving 90 grams of $H_2C_2O_4$ to make 1 litre solution is by definition 1 formal. The molar concentration will be less than one because oxalic acid undergoes dissociation to the extent of about 22 per cent. Therefore, the concentration $H_2C_2O_4$ species in this solution will be 0.78 molar only.

Normality. The normality, N of a solution expresses the number of equivalents of dissolved solute contained in one litre. A gram-equivalent weight of an acid or a base is that weight (in grams) of the solute that will furnish or react with one gram-formula weight of hydrogen ions. Since an equivalent weight is a large quantity, it is more often covenient to refer to a smaller quantity, the milliequivalent weight.

The value of normality of a solution or that of equivalent weight of a solute depends mainly upon the reaction which the solute undergoes. Consider orthophosphoric acid, H_3PO_4, the normality of which varies depending upon the number of protons which it loses. It may lose three, two or one protons depending upon the conditions of the reaction

$$H_3PO_4+OH^- \longrightarrow H_2PO_4^-+H_2O$$
$$H_3PO_4+2OH^- \longrightarrow HPO_4^{2-}+2H_2O$$
$$H_3PO_4+3OH^- \longrightarrow PO_4^{3-}+3H_2O$$

For the calculation of normality the exact nature of the intended chemical reaction must be clearly understood.

The following mathematical relationships which serve as basis for computation in volumetric analysis are derived directly from the definition of a normal solution.

The product of normality by volume in litres is the number of gram-equivalent weights of the solute. Thus 2 litres of a 1.5*N* solution of a reagent contain a total of $2 \times 1.5 = 3$ gram-equivalent weights of the solute.

The product of millilitres (V) and normality represents not only the number of gram weights of solute contained in the given solution, but also the number of gram weights of another substance that will react with the first, or that is chemically equivalent to the first. The relations may be written as :

$n_A \times V_A$ = number of gram weights of *A*

$n_B \times V_B$ = nnmber of gram weights of *B*

where the subscript *A* and *B* indicate the different substances. In the same type of reactions. the number of gram weights of *A* and *B* must be the same. Therefore,

$$n_A \times V_A = n_B \times V_B$$

when any three of these terms in the above relation are known, the fourth can be readily calculated.

2.2. OXIDATION-REDUCTION TITRATIONS

The equivalent weight of a substance is that weight which will consume or produce, chemically equivalent to 1 mole of electrons. The numerical value of the equivalent weight is conveniently found by dividing the molecular weight of the substance by the change in the oxidation number of the substance. The value of the equivalent weight is determined by its reaction and several equivalent weights can exist for the same compound. The reactions of potassium permanganate in different media suggest the different equivalent weights.

Acidic Medium

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$$

Neutral Medium

$$MnO_4^- + 2H_2O + 3e^- \rightleftharpoons MnO_2 + 4OH^-$$

Strongly alkaline Medium

$$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$$

Here in each case the manganese ion has an initial oxidation number of +7. The final oxidation numbers are: +2, +4, and +6 respectively. The equivalent weight of permanganate ion is thus :

Medium	*Change in Oxidation Number*	*Equivalent weight*
Acid	5	$\frac{\text{mol. wt. of } KMnO_4}{5} = \frac{158}{5} = 31.6$
Neutral	3	$\frac{\text{mol. wt. of } KMnO_4}{3} = \frac{155}{3} = 52.66$
Alkaline	1	$\frac{\text{mol. wt. of } KMnO_4}{1} = 158$

For a balanced titration reaction, the equivalent weight is determined by the change in oxidation number only. The number of moles of the substance in the reaction does not enter into it, i.e.,

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$$\underset{+7}{MnO_4^-}+\underset{+2}{Fe^{2+}}+8H^+\rightleftharpoons \underset{+2}{Mn^{2+}}+\underset{+3}{5Fe^{3+}}+4H_2O$$

$$\therefore \text{ Equivalent weight of } KMnO_4=\frac{\text{mol. wt. of } KMnO_4}{5}$$

$$\text{Equivalent weight of } Fe^{2+} = \frac{\text{mol. wt. of } Fe^{2+}}{1}$$

2.3. PRECIPITATION AND COMPLEX-FORMATION TITRATIONS

The equivalent weight of an anion participating in this type of reaction is defined as the weight that will furnish, react with, or be chemically equivalent to 1 gram-atom of a univalent cation, or one-half a gram-atom of a divalent cation, etc. The equivalent weight of cation is the molecular weight of the cation divided by the charge on the ion.

For example:

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow \qquad \text{Eq. wt. } Ag^+ = \frac{\text{Mol. wt.}}{1}$$

$$\text{Eq. wt. } Cl^- = \frac{\text{Mol. wt.}}{1}$$

$$Ca^{2+} + 2F^- \rightarrow CaF_2\downarrow \qquad \text{Eq. wt. } Ca^{2+} = \frac{\text{Mol. wt.}}{2}$$

$$\text{Eq. wt. } F^- = \frac{\text{Mol. wt.}}{1}$$

The cation referred to in the definition is the cation participating directly in the reaction and not necessarily that in the compound whose equivalent weight is being determined. In the reaction

$$Ba^{2+} + CrO_4^{2-} \rightleftharpoons BaCrO_4\downarrow$$

The equivalent weight of some compounds which may be used in the reaction are:

Compound	*Equivalent weight*
Ba^{2+}	$\frac{\text{Mol. wt. of } Ba^{2+}}{2}$
$Ba_3(PO_4)_2$	$\frac{\text{Mol. wt. of } Ba_3(PO_4)_2}{6}$
K_2CrO_4	$\frac{\text{Mol. wt. of } K_2CrO_4}{2}$
$K_2Cr_2O_7$	$\frac{\text{Mol. wt. of } K_2Cr_2O_7}{4}$

Weight of solute in a given weight of solvent of solution. The most commonly employed methods are: (*i*) molality, (*ii*) Percentage Composition and (*iii*) Parts per million.

Molality. A molal solution contains one mole of solute dissolved in 1000g of solvent. This differs from molar solution in that the ratio of solute to solvent is determined by weight.

Percentage composition. The percentage concentration of a solution is the weight in grams of the solute contained in 100g of the solution. It may also indicate the volume of concentrated liquid solute in a given volume of solvent. For example 20 ml of glacial acetic acid diluted in water to 100 ml is known as 20 per cent solution of acetic acid.

Percentage composition may indicate weight of solute in 100 ml of solution. For example 15 grams of KOH dissolved in 100 ml of water is a 15 per cent solution. Other concentration units such as mole ratios, mole fractions and mole percentages are also employed in some cases.

Parts per million. Concentrations of very dilute solutions are conveniently expressed in parts per million (ppm)

$$\text{ppm} = \frac{\text{weight of solute}}{\text{weight of solution}} \times 10^6$$

The distinction between weight and volume of solution is not normally made in very dilute aqueous solutions. Parts per million then are milligrams of solute per litre of solution. To illustrate—a 5 ppm chloride solution contains 5milligram chloride per litre.

Titer. The titer of a solution is the weight of a substance equivalent to a unit volume of the solution. The substance need not to be the solute substance itself, but may be a sought-for substance titrated by the solution, or a substance verivable from the solution.

$$\text{Titer} = \frac{\text{grams of substance}}{\text{litres of solution}} = \frac{\text{mg. of substance}}{\text{ml. of solution}}$$

The titer is a volumetric chemical factor, with which the amount of sought-for substance may be directly calculated from the volume of standard solution for its titrations without any consideration of knowledge of the chemical process that occur in the analysis. It significantly reduces reproducible errors that occur in both the standardization and the analysis.

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2.4. CLASSIFICATION OF METHODS OF VOLUMETRIC ANALYSIS

The reactions used in volumetric analysis belong to various types. Accordingly, volumetric determinations can be subdivided into the following principal methods:

1. Neutralization-Method (Acidimetry and Alkalimetry).
2. Oxidation-Reduction Methods (Redox Titrations).
3. Precipitation Titrations.
4. Complex Formation Titrations.

2.4.1 Neutralization Method (Acidimetry and Alkalimetry)

Acid-base titrations in aqueous solutions are essentially based on the reaction between hydrogen and hydroxyl ions to form water which is ionized to a very slight extent. The net equation for the reaction is given as,

$$H^+ + OH^- \rightleftharpoons H_2O$$

or, if hydronium ion (H_3O^+) is used in place of hydrogen ion, the reaction is,

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O$$

According to the simplest definition, an acid is a hydrogen-containing substance that dissociates into H^+ and an anion when dissolved in water, and a base as a hydroxyl compound that gives a cation and hydroxyl ion in water. The strength of an acid or base depends on the degree of dissociation. Strong acids and bases can be considered to be completely dissociated. The incomplete dissociation of weak acids and bases is characterised by the usual equilibrium expressions. For example, for monoprotic acid, HA

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \ldots (1)$$

The dissociation constant, K_a, is a physical constant characteristic of the particular weak acid, at a given temperature. Similarly, for a base BOH, K_b can be given as,

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad \ldots (2)$$

Writing the equation for the water equilibrium in the form,

$$H_2O \rightleftharpoons H^+ + OH^-$$

The product of the concentrations of these ions at a given temperature is (approximately) constant. At 22°C,

$$[H^+][OH^-] = K_{H_2O} = 10^{-14} \qquad \ldots (3)$$

Since, it is more convenient to represent the reaction of a solution by their negative logarithms instead of the actual concentrations of H^+ or OH^- ions. Therefore, if we take logarithms of equation (3) and reverse the signs, we have

$$-\log[H^+]-\log[OH^-]=14$$

It is customary to refer to hydrogen-ion concentration in terms of pH. Sorenson suggested the notation,

$$pH=\log\frac{1}{[H^+]}=-\log[H^+]$$

From this it follows that,

$$pOH=\log\frac{1}{[OH^-]}=-\log[OH^-]$$

and, $pH+pOH=14$

If an acid is added to pure water, the water equilibrium is disturbed so that $[H^+]$ and $[OH^-]$ are no longer equal. The product must remain constant, as 10^{-14} and hence the $[OH^-]$ diminishes as the $[H^+]$ increases. On the other hand, if a base is added to water, the $[H^+]$ of the water must decrease as the $[OH^-]$ increases. Thus, to define the acidic or basic character of an aqueous solution at room temperature, it is essential to have a knowledge of $[H^+]$ concentration, i.e.,pH value.

(*a*) A solution is acidic if the pH is less than 7.

(*b*) A solution is basic if the pH is greater than 7.

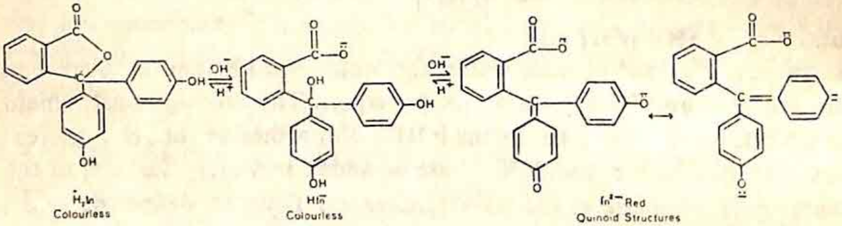
A solution of 7 pH is considered as neutral, as at this pH =

$$[H^+]=[OH^-]$$

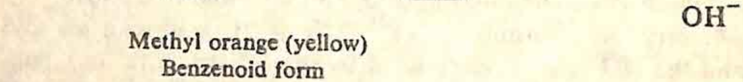
For acidimetry, a solution of any acid is titrated with an alkaline solution, the $[OH^-]$ ions of the latter combine with the H^+ ions of the acid and the concentration of the latter gradually decreases while the pH of the solution increases. At a certain definite pH value the equivalence point is reached and no more alkali should be added.

In alkalimetry, a solution of an alkali is titrated with an acid solution and the OH^- ions are removed by the H^+ ions and the concentrations of the latter gradually increases while the solution pH decreases. At certain definite pH value the equivalence point is reached and the titration must be ended at that point.

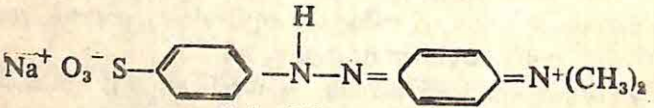
Determination of the equivalence-point. Neutralization is not accompanied by visible changes such as alteration in the colour of the solution. Therefore, a suitable indicator must be added to the titrated solution in order to determine the equivalence point. The equivalence point in neutralization titrations occurs at a definite pH value. Therefore, substances which change colour in accordance with pH are used as neutralization indicators. The indicators used in neutralization titrations are complex organic compounds, which are themselves weak acids or bases. They, like other weak acids and bases, therefore, associate or dissociate, according to the pH of the solution. The well known indicator phenolphthalein is a diprotic acid and is colourless. It dissociates first to a colourless form then, on loosing the second hydrogen, to an ion with a conjugated system, a red colour results.



Methyl orange, another widely used indicator, is a base and is yellow in the molecular form. Addition of a hydrogen ion gives a cation which is pink in colour.



Methyl orange (yellow)
Benzenoid form



Quinoid form
(Pink)

For simplicity, an acid indicator may be designated as HIn and basic indicator as InOH. We can write the equilibrium relationships for an acid indicator as,

$$\underset{\text{Acid colour}}{HIn} \rightleftharpoons \underset{\text{Base colour}}{H^+ + In^-}$$

and for a basic indicator as

$$\underset{\text{Base colour}}{InOH} \rightleftharpoons \underset{\text{Acid colour}}{OH^- + In^+}$$

Indicator range. Neutralization indicators change colour on introduction of $[H^+]$ or $[OH^-]$ ions into their solutions. However, introduction of these ions obviously alters the solution pH. Therefore, we can say that the colour of an indicator depends on pH and therefore, such indicator can be described as pH-indicators. These indicators show a sharp change in colour over a definite narrow range of pH i.e., the indicator is useful over this definite range of pH. This range is called 'indicator-range' and depends only on the properties of the given indicator and is quite independent of the nature of reacting acid or base. Table 2.1 shows some acid base indicators together with their approximate ranges.

TABLE 2.1
Some Acid-Base Indicators

Indicator	*Colour change*		*pH range*
	Acid	*Alkali*	
Thymol blue	Red	Yellow	1.2-2.8
Methyl yellow	Red	Yellow	2.9-4.0
Bromphenol blue	Yellow	Blue	3.0-4.6
Methyl Orange	Red	Yellow	3.1-4.4
Methyl red	Red	Yellow	4.2-6.2
Litmus	Red	Blue	4.5-8.3
Methyl purple	Purple	Green	4.8-5.4
Bromocresol purple	Yellow	Purple	5.2-6.8
Bromothymol blue	Yellow	Blue	6.0-7.6
Phenol red	Yellow	Red	6.8-8.4
Phenolphthalein	Colourless	Red	8.0-9.6
Alizarin yellow R.	Yellow	Violet	10.1-12.0
1, 3, 5,-trinitro-benzene	Colourless	Orange	12.0-14.0

Selection of proper indicator. The choice of an indicator to mark the equivalence point in a titration is governed by essentially the same principle as those governing titration to a fixed pH. An indicator may be used most satisfactorily if the pH changes rapidly in the region of the equivalence point, so that the titration error is till small then if there is inadvertently a difference of a pH unit or so between the end point and the equivalence point. As a general rule, one should select an indicator which changes colour at approximately the pH at the equivalence point of the titration. For weak acids, the pH at the equivalence point is above 7 and phenolphthalein is the usual choice.

For weak bases, where the pH is below 7, methyl red or methyl orange is widely used. For strong acid and strong base, methyl red, bromothymol blue, and phenolphthalein are suitable.

Weak acid with weak base, or *vice-versa* is not a practical interest, since this is always possible to choose a strong acid or strong base for the preparation of a standard solution. Further, such titration would not be precise, for the pH-curve would not be at all steep in the region of the equivalence point. The salt of a weak acid and a weak base is really a buffer, which does not change appreciably in pH on the addition of acid or base.

EXPERIMENTS

Exercise 2.1. *Determine the strength of commercial hydrochloric acid, 10ml of which have been dissolved per litre of the given solution.*

Requirement. Reagent-grade Na_2CO_3.

Reactions. $HCl + Na_2CO_3 \longrightarrow NaHCO_3 + NaCl$

$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$

Ionically. $CO_3^{2-} + H^+ \longrightarrow HCO_3^-$

$HCO_3^- + H^+ \longrightarrow H_2O + CO_2$

Indicator. Methyl Orange.

End point. Yellow to red (acid soln. in the burette).

Procedure. As the given solution of HCl is having 10ml of commercial HCl (nearly 10N) in 1000ml. Hence, the standard solution to be prepared should have nearly same normality.

(*i*) *Preparation of 0.1N solution of sodium carbonate.* Dry 1.2-1.4g of reagent grade Na_2CO_3 in a weighing-bottle at 150-160°C for 2 hours. Cool and store the loosely stoppered bottle in the desiccator. Weigh out nearly but accurately 1.325g of the dried Na_2CO_3, by method of difference. Transfer quantitatively to the calibrated 250ml volumetric flask. Add 40-50ml of distilled water and stir gently to dissolve the solid. Then make up the volume upto 250ml and mix well. This is standard Na_2CO_3 solution whose normality can be calculated by considering the amount transferred to volumetric flask.

(*ii*) *Titration.* Rinse and fill the burette with given acid solution. Remove the air bubbles and set it at zero mark. Pipette out 20ml of the standard Na_2CO_3 solution into a 100ml titration flask and add 2 or 3 drops of methyl-orange. Titrate with the HCl to a sharp colour change, i.e., till red colour is obtained. Repeat the titration with every 20ml of the sodium carbonate solution until three concordant readings are obtained.

Observations. Weight of the weighing bottle, w_1 = ... *g*

wt of weighing bottle + Sodium carbonate, w_2 = ...*g*

wt of weighing bottle after transferring the salt, w_3 = ... *g*

wt of sodiun carbonate transferred to the volumetric flask $=(w_2-w_3)g$

volume of solution made = 250ml.

Volume of Na_2CO_3 solution taken for each titration = 20ml.

Burette readings: Titration of Na_2CO_3 versus HCl.

Sl. No.	*Initial reading*	*Final reading*	*Vol. of HCl (ml)*
1.	...	...	...
2.	...	...	...
3.	...	...	...
4.	...	...	...
5.	...	...	...

Concordant reading.........ml

Calculations.

Normality of Na_2CO_3 solution $= \frac{4\times(w_2-w_3)}{53}$.

To calculate normality of dil HCl solution, apply normality question,

$$N_{HCl}\times V_{HCl}=N_{Na_2CO_3}\times V_{Na_2CO_3}$$

$$\text{or}\quad N_{HCl}=\frac{N_{Na_2CO_3}\times V_{Na_2CO_3}}{V_{HCl}}$$

$$=\frac{N_{Na_2CO_3}\times 20}{V_{HCl}}$$

: Strength of dilute HCl solution

$$= N_{HCl} \times 36.5 g/l \text{ (strength } = \text{Normality} \times \text{Eq. wt.)}$$

Since, commercial HCl was diluted 100 times (10ml in 1000 ml), the strength of commercial HCl can be obtained by multiplying the strength of dil HCl by 100.

Hence, strength of commercial HCl $= N_{HCl} \times 36.5 \times 100$ g/l

Result: Strength of commercial HCl is..............g/l

correct value..................g/l

% Error = ...g/l

Exercise 2.2. *Determine the number of moleculee of water of crystallization in washing soda ($Na_2CO_3 . nH_2O$) provided 0.1N – HCl.*

Reactions. $Na_2CO_3 . nH_2O + 2HCl \rightarrow 2NaCl + (n+1)H_2O + CO_2$

Ionically. $CO_3^{2-} + 2H^+ = H_2O + CO_2$

Indicator. Methyl Orange.

End point. Yellow to red (acid solution in the burette)

Procedure. Prepare a standard solution of $Na_2CO_3 . nH_2O$ (*see* Exercise 2.1) Rinse and fill the burette with given 0.1N HCl solution. Pipette out 20ml of the Na_2CO_3 solution into a conical flask and add 1-2 drops of methyl orange indicator. Add HCl solution from the burette till a permanent red colour is obtained. Repeat till three concordant readings are obtained.

Observations.(*See* Exercise 2.1)

Calculations. Let V be the volume of HCl required to neutralize 20ml of washing soda solution.

Applying normality equation, the normality of washing soda

$$= \frac{0.1 \times V}{20} = 0.005V$$

Molecular-weight of the washing-soda

$$= 106 + 18n$$

$$\text{Eq. wt of } Na_2CO_3 . nH_2O = \frac{106 + 18n}{2}$$

Strength of washing soda solution = Normality × Eq. wt.

$$= 0.005 \times V \times \frac{106 \times 18n}{2} \text{ g/l.}$$

$$= 0.005V\,(53 + 9n). \text{ g/l}$$

But the actual strength of washing soda

$$= \frac{4(W_2 - W_3)}{53} \text{ g/l} \quad \text{(from weighing)}$$

$$\therefore \quad 0.005V\,(53 + 9n) = \frac{4(W_2 - W_3)}{53}$$

or $$n=\frac{1}{9}\left(\frac{4(W_2-W_3)}{53\times 0.005V}-53\right)$$

Result. The number of molecules of water of crystallization in washing-soda= . . . .

Exercise 2.3. *Find out separately the amounts of sodium carbonate and sodium hydroxide present per litre of the given solution, provided $\simeq$0.1N HCl solution.*

Reactions. As the mixture contains NaOH and Na_2CO_3, this will react with HCl in the following way.

$$NaOH+HCl\longrightarrow NaCl+H_2O \qquad \ldots(I)$$

$$\left.\begin{array}{l} Na_2CO_3+HCl\longrightarrow NaHCO_3+NaCl \\ NaHCO_3+HCl\longrightarrow NaCl+H_2O+CO_2 \end{array}\right\} \qquad \ldots(II)$$

Ionically. $$OH^-+H^+\longrightarrow H_2O \qquad \ldots(I)$$

$$\left.\begin{array}{l} CO_3^{2-}+H^+\longrightarrow HCO_3^- \\ HCO_3^-+H^+\longrightarrow CO_2+H_2O \end{array}\right\} \qquad \ldots(II)$$

For the analysis of this mixture two methods may be used:

(1) Warder's method (using two indicators)

(*a*) *Methyl orange.* This gives the end point when whole of sodium hydroxide and whole of sodium carbonate are neutralized, as the pH range of methyl orange covers the both equivalence points.

(*b*) *Phenolphthalein.* From the reactions it is clear that Na_2CO_3 first gives $NaHCO_3$, which reacts further with equal amount of HCl to give equivalence point. This conversion of Na_2CO_3 into $NaHCO_3$ may be regarded as half neutralization of Na_2CO_3. Hence, if phenolphthalein is used as an indicator instead of methyl orange, the end point is obtained when whole of NaOH and half of carbonate is neutralized.

Procedure (*a*) *Preparation of 0.1N Na_2CO_3 solution.* A standard solution of Na_2CO_3 is prepared as in exercise 2.1.

(*b*) *Standardisation of given$\simeq$0.1N HCl.* The given solution of HCl is titrated against above prepared solution of Na_2CO_3 using methyl orange as indicator till a red colour is obtained.

(*c*) *Titration of mixture with acid.* Pipette out 20ml of the given solution containing NaOH and Na_2CO_3 and add 2 or 3 drops of the methyl orange indicator. Titrate it with acid to obtain a permanent red colour.

Again, titrate 20ml of the given mixture solution with the same acid solution using phenolphthalein indicator until the initial pink colour disappears.

Observations. Same as given in exercise 2.1.

Burette readings. (*a*) Standard sodium carbonate Vs. given HCl. Indicator = Methyl orange; End point = Yellow to red.

Sl. No.	*Initial reading*	*Final reading*	*Volume of HCl (ml)*
1.	...	...	...
2.	...	...	...
3.	...	..	...
4.	...	...	...
5.	...	...	...

Concordant Reading .... Vml

(*b*) Titration of given mixture versus HCl solution.
Indicator = Methyl orange
End Point = Yellow to red.

Sl. No	*Initial reading*	*Final reading*	*Volume of HCl (ml)*
1.	...	...	...
2.	...	...	...
3.	...	...	...
4.	...	...	...
5.	...	...	...

Concordant reading = V_1ml

(*c*) Given mixture v/s HCl.
Indicator = Phenolpathalein; End Point = Red to colourless.

Sl. No.	*Initial reading*	*Final reading*	*Volume of HCl (ml)*
1.	...	...	...
2.	...	...	...
3.	...	...	...
4.	...	...	...
5.	...	...	...

Concordant reading = V_2ml

Calculations. Normality of standard Na_2CO_3 solution

$$=\frac{4\times(W_2-W_3)}{53}$$

$$\text{Normality of given HCl}=\frac{N_{Na_2CO_3}\times V_{Na_2CO_3}}{{}^{V}HCl}$$

$$=\frac{4\times(W_2-W_3)}{53}\times\frac{20}{V}=N_1\ \text{(say)}$$

Strength of Na_2CO_3 in the mixture;

Volume of HCl required for the complete neutralization of Na_2CO_3 in 20 ml mixture solution $=2(V_1-V_2)$ ml

$${}^{N}Na_2CO_3=\frac{N_1\times 2(V_1-V_2)}{20}=\frac{N_1(V_1-V_2)}{10}$$

Hence, strength of sodium carbonate in the given mixture

$$=\text{Normality}\times\text{Eq. wt.}$$

$$=\frac{N_1(V_1-V_2)}{10}\times 53\ g/l$$

Strength of NaOH in the mixture;

Volume of HCl required for the complete neutralization of NaOH present in 20 ml of the given mixture.

$$=(2V_2-V_1)\ \text{ml.}$$

$${}^{N}NaOH=\frac{{}^{N}HCl\times{}^{V}HCl}{{}^{V}NaOH}=\frac{N_1\ (2V_2-V_1)}{20}$$

Hence, strength of sodium hydroxide in the given mixture

$$=\text{Normality}\times\text{Eq. wt.}=\frac{N_1(2V_2-V_1)}{20}\times 40$$

$$=2N_1\ (2V_2-V_1)\ g/l$$

(2) Winkler's method. This method involves the separation of carbonate as insoluble barium carbonate by adding excess of $BaCl_2$ solution. The following procedure is applied.

(*i*) The total strength of NaOH and Na_2CO_3 is determined by titrating with standardized HCl solution using methyl orange as indicator.

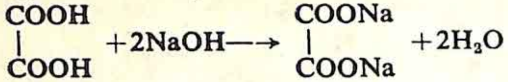
(*ii*) To a known volume of the given mixture excess of $BaCl_2$ is added to precipitate out carbonate as barium carbonate.

$$Na_2CO_3+BaCl_2\longrightarrow 2NaCl+BaCO_3$$

The remaining NaOH is then titrated against HCl solution using phenolphthalein as indicator, knowing the volumes of HCl required for the neutralization of NaOH and Na_2CO_3, their strengths can be calculated by applying the usual method of calculations.

Exercise 2.4. *Estimate the amount of anhydrous oxalic acid present per litre of the given solution; provided $\simeq 0.1$ NNaOH solution.*

Reactions.

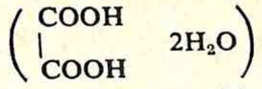


$$\begin{array}{c}\text{COOH}\\ |\\ \text{COOH}\end{array} + 2NaOH \longrightarrow \begin{array}{c}\text{COONa}\\ |\\ \text{COONa}\end{array} + 2H_2O$$

Ionically. $H^+ + OH^- \longrightarrow H_2O$

Indicator. Phenolphthalein.

End point. Appearance of permanent red colour (NaOH solution in the burette).

Procedure. (*1*) *Preparation of the standard solution of oxalic acid.* First calculate how much oxalic acid  $\left(\begin{array}{c}\text{COOH}\\ |\\ \text{COOH}\end{array}\ 2H_2O\right)$ should be taken. A gram-molecule (126 g) of oxalic acid reacts with two gram-molecules of NaOH. Its gram equivalent is therefore $\frac{126}{2} = 63$.

Therefore, the amount required for 250 ml of 0.1 N solution

$$= \frac{63 \times 250 \times 0.1}{1{,}000} = 1.575$$

It is not necessary to weigh out exactly the calculated amount, this is of no advantage and takes much time. Weigh out 1.5-1.6 g of oxalic acid on analytical balance, put it in a weighing bottle and weigh the bottle with oxalic acid accurately. Tip the oxalic acid out carefully through a dry funnel into a thoroughly washed measuring flask. Now weigh the bottle with any remaining grains of oxalic acid accurately again, and by difference find the weight of acid transferred to the flask. Wash all the acid carefully out of the funnel into the flask in a stream of distilled water from a wash-bottle. Add more water, remove the funnel and smoothly swirl the contents of the flask until the oxalic acid dissolves. Make up the volume upto the mark. Towards the end add water drop by drop keeping the eye level with the mark until the bottom of the meniscus touches the mark. Stopper the flask and mix the contents thoroughly by repeatedly inverting and shaking the flask.

(2) *Standardization of NaOH solution.* Pipette out 20 ml of the above prepared oxalic acid solution in a 100 ml conical flask and add 2 or 3 drops of phenolphthalein indicator. Titrate with the given solution of NaOH until a light red colour is obtained and persists for 20 seconds. Repeat the titration until three concordant readings are obtained.

(3) *Titration of NaOH solution with given oxalic acid solution.* Pipette out 20 ml of given oxalic acid solution into the well cleaned conical flask and add two drops of phenolphthalein indicator. Run in the NaOH solution from the burette to obtain a light red colour. Repeat the titration to get at least three concordant readings.

Observations

Weight of the weighing-bottle, $W_1 = \ldots$ g
Weight of weighing-bottle + oxalic acid, $W_2 = \ldots$ g
Weight of the bottle after transferring the acid, $W_3 = \ldots$ g
Weight of the oxalic acid transferred to measuring flask
$= (W_2 - W_3)$ g.
Volume of oxalic acid taken for each titration = 20 ml
Burette readings:

Titration of standard oxalic acid with NaOH solution

Sl. No.	*Initial reading*	*Final reading*	*Volume of NaOH (ml)*
1.	...	...	...
2.	...	...	...
3.	...	...	...
4.	...	...	...
5.	...	...	...

Concordant reading $V_1 = \ldots$ ml

Titration of given oxalic acid solution with NaOH solution

Sl. No.	*Initial reading*	*Final reading*	*Volume of NaOH (ml)*
1.	...	...	...
2.	...	...	...
3.	...	...	...
4.	...	...	...
5.	...	...	...

Concordant reading $V_2 = \ldots$ ml

Calculations. (*i*) Normality of self-prepared oxalic acid solution

$$=\frac{4\times(W_2-W_3)}{63}$$

(*ii*) Normality of NaOH =

$$N_{\text{NaOH}}\times V_{\text{NaOH}}=N_{\text{acid}}\times V_{\text{acid}}$$

$$N_{\text{NaOH}}=\frac{N_{\text{acid}}\times V_{\text{acid}}}{V_{\text{NaOH}}}=\frac{4\times(W_2-W_3)}{63}\times\frac{20}{V_1}$$

(*iii*) Normality of given oxalic acid =

$$N_{\text{acid}}\times V_{\text{acid}}=N_{\text{NaOH}}\times V_{\text{NaOH}}$$

$$N_{\text{acid}}=\frac{N_{\text{NaOH}}\times V_{\text{NaOH}}}{V_{\text{acid}}}=\frac{4\times(W_2-W_3)}{63}\times\frac{20}{V_1}\times\frac{V_2}{20}$$

Strength of oxalic acid = Normality × Eq. wt.

$$=\frac{4\times(W_2-W_3)}{63}\times\frac{V_2}{V_1}\times 63$$

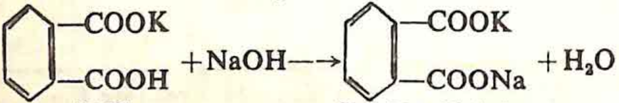
$$=4\times\text{weight of oxalic acid taken for 250 ml.}\times\frac{\text{volume of NaOH with given oxalic acid}}{\text{volume of NaOH with standard oxalic acid}}$$

Result = . . . *g/l*, **Correct value** = ... *g/l*, % **Error** = ... *g/l*

Exercise 2.5. *Determine the molecular weight of a dibasic acid 5 g of which have been dissolved per litre of the given solution, provided≃0.1N-NaOH. Prepare a standard solution of potassium hydrogen phthalate (KHP).*

Reactions. $2NaOH+H_2A\longrightarrow Na_2A+2H_2O$

(dibasic acid)



(KHP) Sod. Pot. Phthalate

Ionically. $H^++OH^-\longrightarrow H_2O$, *Indicator.* Phenolphthalein,

End point. Appearance of permanent light red colour (NaOH solution in the burette)

Procedure. (*i*) *Preparation of standard solution of* (*KHP*). Calculate the weight required of potassium hydrogen phthalate (formula $KHC_8H_4O_4$, mol. wt. 204.2), for the preparation of 0.1N solution in 250 ml.

$$=\frac{204.2}{1{,}000}\times 250\times 0.1=5.105\text{ g}$$

Transfer approximately 6 g of the potassium hydrogen phthalate (previously dried at 110°C for one hour) to a weighing bottle. Weigh accurately by the method of difference between 4.9 and 5.1 g of the solid into a 250 ml beaker. To this add 100 ml of distilled water and heat on a hot-plate to dissolve all the solid. Cool and transfer to a 250 ml measuring flask, using a long stem funnel and pouring the solution down a stirring rod to prevent splashing. Rinse the beaker several times with portions of distilled water, transferring the rinsings to the volumetric flask. Rinse the funnel well and make upto the mark on the flask with distilled water. This is done by adding distilled water until the level is just below the calibration mark and now add water with a pipette until the meniscus is exactly on the mark, mix the contents of the flask thoroughly.

(*ii*) *Standardization of 0.1N NaOH using the above prepared KHP solution.* Wash and rinse the burette with the sodium hydroxide solution provided and then fill. Pipette out 20 ml of KHP solution into a 100 ml conical flask and add two drops of phenolphthalein indicator. Titrate with NaOH solution until red colour is obtained and persists for 15-20 seconds. Repeat to get concordant readings.

(*iii*) *Standardization of unknown acid solution.* Pipette out 20 ml of the given dibasic acid solution into the titration flask. Add 1-2 drops of phenolphthalein as an indicator. Titrate it with NaOH solution until a light red colour is obtained. Repeat to get three concordant readings.

Wash the burette thoroughly after using sodium hydroxide. A trace of hydroxide left on the tap can cause seizure of the joint.

Observations. Weight of the weighing-bottle, $W_1 = \ldots$ g

Weight of weighing bottle + Salt, $W_2 = \ldots$ g

Weight of weighing bottle after the transfer of salt, $W_3 = \ldots$ g

Weight of salt transferred to the measuring flask $= (W_2 - W_3)$ g

Capacity of the pipette = 20 ml.

Burette readings

Titration of KHP solution with NaOH solution

Sl. No.	*Initial reading*	*Final reading*	*Volume of NaOH (ml)*
1.	...	...	...
2.	...	...	...
3.	...	...	...
4.	...	...	...
5.	...	...	...

Concordant reading $V_1 = \ldots$ ml

Titration of dibasic acid solution with NaOH solution

Sl. No.	*Initial reading*	*Final reading*	*Volume of NaOH (ml)*
1.	...	...	...
2.	...	...	...
3.	...	...	...
4.	...	...	..
5.	...	...	...

Concordant reading $V_2 = \ldots$ ml

Calculations. (*i*) Normality of KHP solution

$$= \frac{4\times(W_2-W_3)}{204.2}$$

(*ii*) Normality of NaOH solution.

$$N_{\mathrm{NaOH}} = \frac{N_{\mathrm{KHP}}\times V_{\mathrm{KHP}}}{V_{\mathrm{NaOH}}} = \frac{4\times(W_2-W_3)}{204.2}\times\frac{20}{V_1}$$

(*iii*) Normality of dibasic acid solution.

$$N_{\mathrm{H_2A}} = \frac{N_{\mathrm{NaOH}}\times V_{\mathrm{NaOH}}}{V_{\mathrm{H_2A}}} = \frac{4\times(W_2-W_3)}{204.2}\times\frac{20}{V_1}\times\frac{V_2}{20}$$

$$= \frac{4\times(W_2-W_3)}{204.2}\times\frac{V_2}{V_1}$$

Equivalent weight of H_2A.

$$= \frac{\text{Strength}}{\text{Normality}} = \frac{5(\text{given})}{4\times(W_2-W_3)}\times\frac{204.2\times V_1}{1 \quad V_2}$$

Since the given acid is a dibasic acid

$$\text{Mol. Wt.} = \text{Eq. Wt.}\times\text{Basicity}$$

$$= \frac{5\times 204.2\times V_1}{4(W_2-W_3)\times V_2}\times 2$$

All the factors on the right hand side are known, hence, the molecular weight can be easily calculated.

DETERMINATION OF THE TOTAL ALKALINE STRENGTH OF SODA ASH

Soda ash is crude sodium carbonate. If made by the ammonia process it may contain also sodium chloride, sulfate, and hydroxide; when made by the Le Blanc process it may contain sodium sulfide, silicate, and aluminate, and other impurities. Some of these, notably the hydroxide, ~~combine~~ with acids and contribute to the total alkaline strength, but it is customary to calculate this strength in terms of sodium carbonate, *i.e.*, as though no other alkali were present.

The analysis of soda ash is chosen merely as a typical alkalimetric process and the student should bear in mind that there are many other types of commercial products which are alkaline in nature and which can be analyzed by a process essentially the same as that given below. Among these products can be included pearl ash (impure K_2CO_3), limestone ($CaCO_3$), quick lime (CaO), commercial caustic soda ($NaOH$), washing powder, and ammonium hydroxide solutions.

Procedure.—Weigh out accurately to four significant figures two samples of soda ash of about one gram each into beakers of flasks of about 200 ml. capacity. Dissolve the ash in 75 ml. of water, warming gently. Cool, add two drops of methyl orange (Note 1) and titrate for the alkali with the standard hydrochloric acid solution, using the standard alkali to complete the titration as already prescribed.

From the volumes of acid and alkali employed, corrected for buret errors and temperature changes, and the data derived from the standardization, calculate the percentage of alkali present, assuming it all to be present as sodium carbonate (Note 2). Also

Notes.—1. The hydrochloric acid sets free carbonic acid which is unstable and breaks down into water and carbon dioxide, most of which escapes from the solution. Carbonic acid is a weak acid and, as such, does not yield a sufficient concentration of H^+ ions to cause the indicator to change to a pink.

2. A determination of the alkali present as hydroxide in soda ash may be determined by precipitating the carbonate by the addition of barium chloride, removing the barium carbonate by filtration, and titrating the alkali in the filtrate

The caustic alkali may also be determined by first using phenolphthalein as an indicator, which will show by its change from pink to colorless the point at which the caustic alkali has been neutralized and the carbonate has been converted to bicarbonate, and then adding methyl orange and completing the titration. The amount of acid necessary to change the methyl orange to pink is a measure of one-half of the carbonate present. The results of the double titration furnish the data necessary for the determination of the caustic alkali and of the carbonate in the sample.

calculate the alkaline strength of the ash in terms of per cent Na_2O (Note 3).

2.4.2. Oxidation reduction titrations

An oxidation-reduction titration is one based on oxidation-reduction reactions. Oxidation-reduction reactions involve a transfer of electrons from a substance which releases electrons to another substance, which accepts them. The process of releasing electrons is oxidation, and the process of accepting electrons is called reduction. *In other words we can say that oxidation is a loss of electrons or de-electronation while reduction is a gain of electrons or electronation.* The following examples illustrate the oxidation, reduction and the oxidation-reduction (redox reaction).

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad \text{(Oxidation)}$$
$$Ce^{4+} + e^- \rightarrow Ce^{3+} \qquad \text{(Reduction)}$$
$$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+} \qquad \text{(Redox reaction)}$$

A substance that decreases in positive oxidation state or acts as an electron acceptor is called an Oxidising agent. A substance that increases in oxidation state or acts as electron donor is known as Reducing agent.

The following terminology is in common use for redox systems:

$$\text{Oxidant} + ne^- \rightleftharpoons \text{Reductant}$$

The oxidant is the substance that gains electrons and reductant the substance that gives electrons.

Oxidising agents and their reduced forms can be arranged in order according to their ability to gain and lose of electrons respectively.

Electrode potential. Place a strip of copper metal in contact with water. The metal copper will tend to dissolve according to the following reaction:

$$Cu \text{ (in contact with water)} \rightarrow Cu^{2+} + 2e^-$$

The electrons released in the above reaction get collected on the copper strip. A difference in potential is thus developed between electrode and the solution. The process of dissolution will continue until the concentration of the charge built up on the metal becomes high enough to begin to attract metal ions from solution to form metal

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3. It is common practice in certain analyses to express percentages in terms of the oxides of the elements. This is particularly convenient in mineral analyses where the exact combinations of the various constituents are often unknown.

atoms and the process is reversed. The electrode potential depends upon: (*a*) the nature of the redox system employed, (*b*) the concentration of the ions present.

Electrode potential thus measures the electron-releasing tendency of redox system. The absolute value of the electrode potential can not be determined because voltage readings are obtained only when two or more half cells are combined. Hence, relative values are only obtained by comparison with the hydrogen electrode which has been assigned a value of zero standard electrodes potential (SEP), when the hydrogen gas at 1 atm pressure is in contact with a piece of platinum and with hydrogen ion concentration at 1M.

The nature of an oxidation-reduction titration can best be studied in terms of electrical phenomena associated with the reaction. The equivalent weight of a reagent in an oxidation-reduction reaction is equal to the molecular weight of the compound (or atomic weight if reagent is an element) divided by the change in the oxidation number, that the reagent undergoes in the reaction. The same substance can have different equivalent weight under different conditions of the reaction. For example, potassium permanganate has three different values of equivalent weights in the following reactions

(*a*) $MnO_4^- + e^- \rightarrow MnO^{2}{}_4{}^-$

$$\text{Equivalent weight of } KMnO_4 = \frac{\text{Molecular weight}}{1}$$

(*b*) $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$

$$\text{Equivalent weight of } KMnO_4 = \frac{\text{Molecular weight}}{3}$$

(*c*) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$$\text{Equivalent weight of } KMnO_4 = \frac{\text{Molecular weight}}{5}$$

Indicators used in oxidation-reduction titrations. The most important types of indicator systems employed are the following:

(*a*) *Redox indicator*. A redox indicator is an oxidation-reduction system in which colour of the oxidised form is different than the colour of the reduced form *i.e.*,

$$\underset{\text{(colour A)}}{\text{Oxidised}} + n\bar{e} \rightleftharpoons \underset{\text{(colour B)}}{\text{Reduced}}$$

The development of redox indicators has helped in extending the application of redox titrations especially those involving dichromate and cerium. Diphenylamine, Ferroin and Nitroferroin are some examples of redox indicators.

(*b*) *Self-indicator*. The most commonly employed self indicator is potassium permanganate. It is intensely coloured but when added to a reducing agent in solution becomes colourless. As soon as all reducing substances have been removed, the next drop of permanganate colours the solution pink. This is taken as the end point or equivalence point.

(*c*) *Starch-iodine indicator*. Iodine forms an intensely blue coloured complex with starch solution. When iodine is used as a titrant a starch solution will remain colourless as long as it is being used in the reaction. The first drop of excess iodine causes the starch to acquire intense blue colour. The change is reversible and this indicator is very widely used.

We shall study the use of three important oxidation-reduction reagents:

1. Potassium Permanganate,
2. Potassium Dichromate,
3. Iodine.

Potassium permanganate. It is very widely used oxidative titrant because it is a strong oxidising agent. In addition potassium permanganate is a self-indicator one drop excess imparts pink colour to the solution. The most common application of potassium permanganate is in acidic medium where it gets reduced to Mn^{++}. The reduction of MnO_4^- to Mn^{++} is a very complex process with the formation of intermediate oxidation states of manganese (+6, +4, +3). This is the most widely used of the permanganate reactions.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Potassium permanganate can not be obtained in pure form and its solution is not very stable, therefore, it is not a primary standard. Acidic and alkaline solutions are less stable than the neutral ones. Solutions of permanganate should be protected from unnecessary exposure to light and should be preferably stored in a dark coloured bottle. Potassium permanganate solutions may be standardised using arsenious oxide or sodium oxalate as primary standard.

Method of the preparation of 0.1N potassium permanganate solution. Dissolve 3.2 gm of highly pure potassium permanganate in 1 litre of water. Heat the solution to boiling and keep this solution for one hour. Filter the solution using pure asbestos or through the sintered glass crucible. Transfer the filterate to a clean glass stoppered bottle and protect this from bright or diffuse light. Filter the solution before use and standardise.

SOME VOLUMETRIC APPLICATIONS OF POTASSIUM PERMANGANATE

Exercise 2.6. *Determine the strength of given oxalic acid solution in grams litre. You are provided with N/10 potassium permanganate solution.*

Principle. Oxalic acid is oxidised by potassium permanganate on heating and the reaction is catalysed by Mn^{2+} and can be symbolised as follows:

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

Ionic equations.

$$[MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$

$$[C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-] \times 5$$

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

Procedure. Pipette out 10 ml of given oxalic acid in a clean conical flask and add to this about 10 ml of dil H_2SO_4. Heat the solution to 60-70°C. Add potassium permanganate solution from the burette in small lots with shaking till it acquires a light pink colour at the end point. Repeat the titration till three concordant readings are obtained. Record your observations as follows:

Volume of oxalic acid taken in a conical flask = 10.0 ml.

Sl. No.	*Burette reading*		*Volume of $KMnO_4$ used (ml)*
	Initial	*Final*	
1.	...	...	...
2.	...	...	...
3.	...	...	...
4.	...	...	...

Method of calculation. Let N_1 be the normality of oxalic acid. For 10 ml of oxalic acid solution let V_2 be the volume of 0.1 N $KMnO_4$ solution used.

$$\therefore \quad N_1 \times 10 = 0.1 \times V_2$$

$$N_1 = \frac{0.1 \times V_2}{10} = 0.01\ V_2$$

Strength of oxalic acid in grams per litre $= N_1 \times$ Equivalent weight

$$= 0.01\ V_2 \times 63 \text{ grams per litre.}$$

Exercise 2.7. *Estimate the available volume of oxygen in the given* *hydrogen peroxide solution. You are provided with N/10 $KMnO_4$ solution.*

Principle. Hydrogen peroxide is marketed in four strengths "10"-, "20"-, "40-" and "100-" volumes concentrations. "10-volume" solution means that a hydrogen peroxide solution when decomposed completely on heating yields 10 times its volume of oxygen measured at 0°C and 760 mm pressure, *i.e.*,

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

$$2 \times 34 \qquad\qquad 22.4 \text{ litres (at S.T.P.)}$$

The above equation indicates that 2 gm-moles per litre (*i.e.*, 68 gm) of H_2O_2 give 1 gm-mole of oxygen (*i.e.*, 22.4 litres at S.T.P.). The reaction of hydrogen peroxide with potassium permanganate can be written as

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

Ionic reaction.

$$[MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O] \times 2$$

$$[H_2O_2 = O_2 + 2H^+ + 2e^-] \times 5$$

$$\overline{2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 5O_2 + 8H_2O}$$

Procedure. Take 10 ml of the given H_2O_2 solution in a 250 ml conical flask add about 100 ml of distilled water and 10 ml of dilute sulphuric acid. Titrate with 0.1N potassium permanganate which is added from the burette in small lots with shaking till the solution acquires light pink colour. The volume of potassium permanganate used is read from the burette. Titration is repeated till we get three concordant readings. The observations are recorded in the same fashion as was done in the previous experiment.

Method of calculations. Since 1 mole of H_2O_2 gives two electrons on decomposition, the equivalent weight of H_2O_2 will be half of its molecular weight *i.e.*, 17 gm. Let N_1 be the its normality and V_2 be the volume of potassium permanganate used for 10 ml of the hydrogen peroxide solution; *i.e*

$$N_1 \times 10 = 0.1 \times V_2$$

$$N_1 = 0.01 V_2$$

Strength of H_2O_2 solution $= 0.01\ V_2 \times 17$ gm/litre.

Since 68 grams per litre solution of H_2O_2 yields 22,400 cc of O_2

$\therefore$ 0.01 $V_2 \times 17$ grams per litre solution of H_2O_2 will give

$$= \frac{22{,}400}{68} \times 0.01\ V_2 \times 17 \text{ cc of } O_2$$

This is also the available volume of oxygen from 1 litre of given

H_2O_2 solution or the available volume of oxygen from 1 ml of given H_2O_2 solution given by the relation

$$=\frac{22,400}{68}\times\frac{0.01\ V_2\times 17}{1,000}\text{ cc}$$

Exercise 2.8. *Determine the strength of Fe^{2+} ions in grams per litre of the given ferrous sulphate solution ($FeSO_4.7H_2O$). You are provided with N/10 $KMnO_4$ solution.*

Principle. Ferrous ion can be titrated with potassium permanganate solution in presence of dilute sulphuric acid. Chloride interfers in the iron titration, should be eliminated from the solution. The addition of a few ml of syrupy phosphoric acid improves the colour change at the end point due to the formation of colourless $Fe(HPO_4)$ product. The chemical reaction can be symbolised as follows:

$$2KMnO_4+3H_2SO_4\longrightarrow K_2SO_4+2MnSO_4+3H_2O+5O$$
$$[2FeSO_4+H_2SO_4+(O)\longrightarrow Fe_2(SO_4)_3+H_2O]\times 5$$
$$\overline{2KMnO_4+10FeSO_4+8H_2SO_4\rightarrow K_2SO_4+2MnSO_4+5Fe_2(SO_4)_3+H_2O}$$

Ionic reaction.

$$MnO_4^-+5e^-+8H^+\longrightarrow Mn^{2+}+4H_2O$$
$$[Fe^{2+}\longrightarrow Fe^{3+}+e^-]\times 5$$
$$\overline{MnO_4^-+5Fe^{2+}+8H^+\longrightarrow 5Fe^{3+}+Mn^{2+}+4H_2O}$$

Procedure. Pipette out 10 ml of ferrous sulphate solution in 100 ml conical flask and add to this about 10 ml of dil. sulphuric acid and 2-3 ml of syrupy phosphoric acid. Add potassium permanganate solution from the burette dropwise with stirring in the cold till the solution acquires light pink colour. This is the end point. Note the volume of potassium permanganate used in this titration. Repeat the titration till two concordant readings are obtained. Record the observations in the note book in the same manner as in the previous experiment.

Method of calculation. Let N_1 be the normality of given ferrous sulphate solution and V_2 ml be the volume of the potassium permanganate required for the complete oxidation of ferrous to ferric state,

$$N_1\times 10=0.1\times V_2$$
$$\therefore\ N_1=\frac{0.1\times V_2}{10}$$

Amount of Fe^{2+} ions in grams per litre of the given solution $=0.01\times V_2\times 56.0$

Potassium dichromate. It is a less powerful oxidising agent than potassium permanganate solution. It can be obtained pure and is stable up to its fusion point, and therefore an excellent primary standard. Potassium dichromate solution is easily reduced by organic matter than potassium permanganate and is also stable towards light. It is not reduced by cold hydrochloric acid provided the acid concentration does not exceed 1 or 2N, therefore, it can be used in the determination of iron in iron ores. In acid medium, the reduction of potassium dichromate can be written as,

$$K_2Cr_2O_7 + 14H^+ + 6e^- \longrightarrow 2K^+ + 2Cr^{3+} + 7H_2O$$

From this equation it follows that the equivalent weight of potassium dichromate is one-sixth of the molecular weight, *i.e.*, $\frac{294.22}{6}$ or 49.037 gm.

For preparing 0.1N solution of potassium dichromate weigh out 4.9037g of pure dry potassium dichromate dissolve in distilled water and dilute to one litre.

Indicators used in potassium-dichromate titration. The end point in potassium dichromate titration is usually determined by using two types of indicators.

(*a*) *External* (*Spot test*) *indicators*. External indicators were once employed when no internal indicator was available. Here the indicator cannot be added to the solution to be titrated, but is placed in the depressions of a white glazed groove-tile (spot-test plate). As the equivalence point is approached a thin glass rod or a glass tube drawn into a fine jet at the end is used to transfer a portion of the reaction mixture from the titration flask to the reagent on the groove-tile. A colour change is observed when the equivalence point is reached. The use of potassium ferricyanide as an external indicator is the best known example in the titration of iron with dichromate. As long as ferrous ion is present in the titration mixture, the indicator will turn blue on the transfer of the solution. The appearance of blue colour is due to the formation of ferro ferricyanide (Turnbull's blue) according to the following reaction:

$$3Fe^{2+} + 2[Fe(CN)_6]^{3-} \longrightarrow \underset{\substack{\text{Turnbull's blue} \\ \text{(Blue-complex)}}}{Fe_3[Fe(CN)_6]_2}$$

When more dichromate solution is added instead of blue colour, a bluish-green then green and ultimately no colour change is observed when the equivalence point has been reached.

(*b*) *Internal* (*redox*) *indicators*. Redox indicators are organic substances which can be reversibly oxidized or reduced, with different colours in the oxidized and reduced forms. For simplicity, let us desi nate the redox couple as follows:

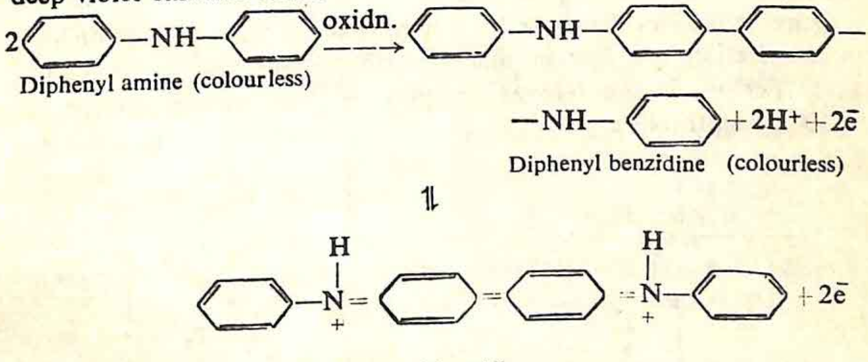
$$\underset{\text{(Colour A)}}{In^+} + e^- \rightleftharpoons \underset{\text{(Colour B)}}{In}$$

Where one electron is gained by the oxidant and no hydrogen ions are involved in the reaction. Let us also say that the colours of the oxidized and reduced forms are different, as indicated above. The equation for the potential of this system is:

$$E = E^\circ_1 - 0.059 \log \frac{[In]}{[In^+]}$$

where E°_i is the standard potential of the indicator couple. For satisfactory use in an oxidation-reduction titration, the reduction potential of the indicator must be close to that of the reduction potentials of the oxidation-reduction system at the equivalence point in the titration. This would result in the sharp change in colour and minimise the indicator error in the titration.

Diphenylamine was one of the first redox-indicators to be widely used in volumetric analysis. Since the compound is sparingly soluble in water, and tungstate ion and mercuric chloride interfere with its action, the barium or sodium salt of diphenyl-amine sulphonic acid is more commonly used. The reduced form of this indicator is colourless and is oxidised by oxidising agents with high oxidation potentials, such as $KMnO_4$, $K_2Cr_2O_7$, $KClO_3$, KNO_2 etc. to give a deep violet oxidized form.



Diphenyl amine (colourless)

Diphenyl benzidine (colourless)

Diphenyl benzidine
(violet)

The presence of a long conjugated system such as that in the diphenylbenzidine ion, leads to absorption of light in the visible region, and hence the ion is coloured.

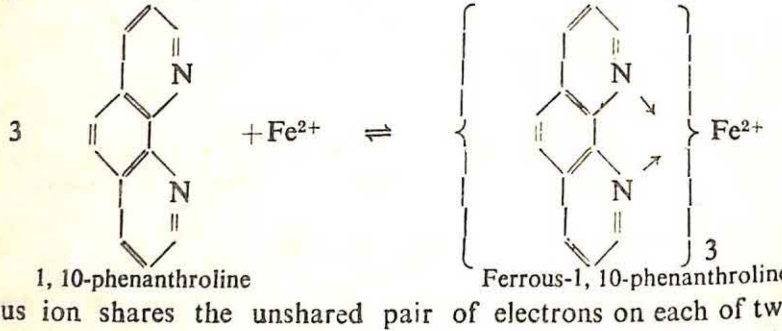
At potentials below 0.73 *V* the reduced form of the indicator (diphenylamine) is predominant, and the solution therefore remains colourless. At E = 0.79 *V* and over, the oxidized form (diphenyl benzidine violet) is predominant and the solution has an intense blue-violet colour. Between 0.73 *V* and 0.79 *V* the colour of the solution changes gradually from colourless to blue-violet. Because of this reason, *i.e.*, potential (0.73 *V* to 0.79 *V*), diphenyl amine is not a suitable indicator in the titration of ferrous ions with permanganate where the change of potential extends from E = 0.944 *V* to E = 1.475*V*. On the other hand, it is highly suitable indicator for the estimation of ferrous ions with dichromate.

$$Cr_2O_7^{2-}+6Fe^{2+}+14H^+\longrightarrow 6Fe^{3+}+2Cr^{3+}+7H_2O$$

In this case the standard reduction potential of the iron system is 0.77 *V* and for the dichromate system is 1.33 *V*. Another commonly used redox indicator in this case is diphenyl amine sulphonate having reduction potential 0.84 volt.

Ferrous ion is titrated with dichromate in a sulphuric phosphoric acid medium, while using diphenyl amine as internal indicator. The presence of considerable phosphoric acid is necessary in order to reduce the concentration of ferric ion by forming a colourless, soluble and stable, $[Fe(PO_4)_2]^{3-}$, complex. Otherwise the ferric ion, because of its tendency to oxidize the indicator, prevents a sharp end point. The addition of preventive solution (phosphoric acid), thus helps in getting a sharp colour change of the indicator at the end point and renders the indicator-error negligible.

Other indicators that have been employed internally in the dichromate titration are ferroin and N-methyl diphenylamine sulphonic acid. Ferroin is the ferrous complex of the organic compound 1, 10-phenanthroline,



1, 10-phenanthroline   Ferrous-1, 10-phenanthroline

Ferrous ion shares the unshared pair of electrons on each of two nitrogen atoms in 1, 10-phenanthroline. Three such molecules of the organic compound attach themselves to the metallic ion to form a blood red complex ion. Ferric ion, formed by the oxidation of ferrous ion, also forms a light-blue coloured complex with three molecules of 1, 10-phenanthroline. Hence, a sharp colour change occurs when ferrous is oxidized to ferric in the presence of 1, 10-phenanthroline

$$\underset{\text{(light blue)}}{Ph_3Fe^{3+}} + \bar{e} \rightleftharpoons \underset{\text{(dark red)}}{Ph_3Fe^{2+}} \qquad E^\circ = 1.06\ V$$

The indicator is prepared by mixing equivalent quantities of ferrous sulphate and 1, 10-phenanthroline. The complex is called ferroin; the complex salt of ferric ions is called ferriin. The colour change occurs at about 1.11*V*, since the colour of ferrion is so much more intense than that of ferriin.

Substituted 1, 10-phenanthrolines also form complexes with ferrous and ferric ions and act as redox indicators. The redox potentials are different from that of the ferroin-ferriin system. Table 2.2 lists some true redox indicators with the colours observed and the "transition" potentials of the redox couple. The transition potentials are the formal potentials of the systems in the media indicated and are usually of more practical value than the standard potentials.

TABLE 2.2.

Transition-Potentials of Some Redox Indicators

Indicator	*Colour of reductant*	*Colour of oxidant*	*Transition potential, Volts*	*Conditions*
Neutral red	Colourless	Red	0-24	1-M H_2SO_4
Methylene blue	Colourless	Blue	0.53	1-M H_2SO_4
Diphenyl amine	Colourless	Violet	0.76	1-M H_2SO_4
Diphenyl benzidine	Colourless	Violet	0·76	1-M H_2SO_4
Diphenylamine sulphonic acid	Colourless	Red violet	0.85	Dilute acid
Erioglaucin A	Yellow Green	Bluish-red	0.98	0.5-M H_2SO_4
Ferroin	Red	Faint blue	1.11	1-M H_2SO_4
Nitroferroin	Red	Faint blue	0.25	1-M H_2SO_4

Exercise 2.9. *Determine the strength of Mohr's salt solution, using* $K_3[Fe(CN)_6]$ *as external indicator. You are provided with* $\simeq$ *0.05N-* $K_2Cr_2O_7$ *solution.*

Theory. Potassium dichromate oxidizes Mohr's salt according to the equation:

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O \text{ (Nascent Oxygen)}$$

$$[2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O] \times 3$$

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

or, *ionically* $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

Ferrous ions, in Mohr's salt $FeSO_4(NH_4)_2SO_4.6H_2O$ only undergo oxidation, the absence of which can be easily observed by no colour change in the yellow colour of the ferricyanide.

Indicator. Potassium ferricyanide solution, which can be prepared by washing repeatedly a small crystal of pure potassium ferricyanide with distilled water in order to remove the superficial coating of any potassium ferricyanide, and then dissolving it in distilled water.

End-point. No change in the yellow colour of the ferricyanide (Potassium dichromate solution in the burette).

Procedure. (*i*) *Preparation of standard solution of Mohr's salt.* Weigh out accurately on an analytical balance about $\frac{392 \times 250}{1000} \times {}^{\cdot}05$ $= 4.9$ *g* of pure sample of Mohr's salt by the method of difference. Transfer it into a 250 ml measuring flask and add 20 ml of dilute H_2SO_4 make up the volume to 250 ml with distilled water and mix thoroughly. Calculate and record the normality of the solution.

(*ii*) *Standardization of given $K_2Cr_2O_7$ solution.* Pipette out 20 ml of the primary standard solution (Mohr's salt) to titration flask and add 15-20 ml of 2N sulphuric acid. Put the $K_2Cr_2O_7$ solution in a burette and adjust the level to the zero mark. If the bottom edge of the meniscus is difficult to see, all the readings may be taken against the top of the meniscus.

Take freshly prepared $K_3[Fe(CN)_6]$ solution and place drops of this solution in the grooves of a porcelain groove-tile. Now titrate the Mohr's salt solution against $K_2Cr_2O_7$ solution. Samples of the titrated solution are withdrawn by means of a glass rod or a glass tube with its end drawn out to a fine capillary, and mixed with drops of the indicator, already taken in the groove-tile. It is also possible to apply drops of the titrated solution on to filter paper which has been soaked in the indicator solution and dried.

During the first titration spot tests are performed at intervals of 1-2 ml until a blue colour is no longer produced with $K_3[Fe(CN)_6]$. This gives a rough estimate of the volume of $K_2Cr_2O_7$ solution needed, in the next titration similar samples are taken only near the end of the titration at intervals of 0.1-0.2 ml. In the third titration the exact volume of $K_2Cr_2O_7$ solution required for the titration is finally found. In this way, the error caused by the removal of part of the solution for the spot tests is made negligibly small. The titration is repeated to get a set of concordant readings.

(*iii*) *Standardization of given Mohr's salt solution.* Pipette out 20 ml of the unknown Mohr's salt solution and acidify this by adding 15-20 ml of 2N sulphuric acid. Titrate it against the $K_2Cr_2O_7$ solution taken in burette as explained in step (2) till concordant readings are obtained.

Observations.

Weight of weighing bottle, $W_1 = \ldots g$.

Weight of weighing bottle + Mohr's salt, $W_2 = \ldots g$.

Weight of weighing bottle after transferring the salt, $W_3 = \ldots g$.

Weight of Mohr's salt transferred to prepare 250 ml of standard solution $= (W_2 - W_3) \times$ g.

Volume of Mohr's salt solution taken for each titration = 20 ml.

Burette readings:

Standard Mohr's salt solution vs. $K_2Cr_2O_7$ solution

Sl. No.	*Initial reading*	*Final reading*	*Vol. of $K_2Cr_2O_7$ (ml)*
1.	0.0	9.0 Blue colour 10.0 No blue colour	9-10
2.	0.0	9.3 Blue colour 9.4 No blue colour	9.3-9.4
3.	0.0	9.4 No blue colour	9.4
4.	...	...	...
5.	...	...	...
6.	...	...	...

Concordant reading $= V_1 \ldots$ ml.

Given Mohr's salt solution vs. $K_2Cr_2O_7$ solution

Sl. No.	*Initial reading*	*Final reading*	*Volume of $K_2Cr_2O_7$ (ml)*
1.	...	...	...
2.	...	...	...
3.	...	...	...
4.	...	...	...
5.	...	...	...

Concordant reading $= V_2 \ldots$ ml.

Calculations.

Normality of self prepared Mohr's salt solution $= \frac{\text{strength}}{\text{Eq. Wt.}} = \frac{4x}{392}$;

where $x = (W_2 - W_3)$ g.

Normality of $K_2Cr_2O_7$ solution

$$N_{K_2Cr_2O_7} \times V_{K_2Cr_2O_7} = N_{\text{Mohr's salt}} \times V_{\text{Mohr's salt}}$$

$$N_{K_2Cr_2O_7} = \frac{N_{\text{Mohr's salt}} \times V_{\text{Mohr's salt}}}{V_{K_2Cr_2O_7}} = \frac{4x \times 20}{392 \times V_1}$$

Normality of given Mohr's salt solution

$$N_{\text{Mohr's salt}} \times V_{\text{Mohr's salt}} = N_{K_2Cr_2O_7} \times V_{K_2Cr_2O_7}$$

$$N_{\text{Mohr's salt}} = \frac{N_{K_2Cr_2O_7} . V_{K_2Cr_2O_7}}{V_{\text{Mohr's salt}}} = \frac{4x \times 20}{392 \times V_1} \times \frac{V_2}{20}$$

Strength of Mohr's salt solution = Normality × Eq.Wt.

$$\frac{4x \times 20\, V_2}{392 \times V_1 \times 20} \times 392 = \frac{4x \times V_2}{V_1} \text{ g/l}$$

or Strength of Mohr's salt solution =

$$\frac{4 \times \text{Wt. of salt transferred to 250 ml flask} \times \text{Volume of } K_2Cr_2O_7 \text{ with given Mohr's salt solution}}{\text{Volume of } K_2Cr_2O_7 \text{ with standard Mohr's salt solution.}} \text{ g/l}$$

Exercise 2.10. *Determine the percentage of iron in the given iron ore by chromatometric method. Use diphenyl amine as internal indicator.*

Principle. The chromatometric method is based on reactions of oxidation by the chromate ion. Its oxidizing action is due to conversion of $Cr_2O_7^{2-}$ anions containing sexivalent chromium into Cr^{3+} cation.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$$

The most important applications of chromatometric method are in determination of iron in ores, slags, alloys, and similar materials. The principal ores of iron are:

(1) Haematite, Fe_2O_3
(2) Magnetite, Fe_3O_4
(3) Geothite, $Fe_2O_3.H_2O$
(4) Limonite, $[Fe_2O_3.H_2O]xH_2O$
(5) Siderite, $FeCO_3$.

When they are dissolved, the iron is usually obtained in the form of Fe^{3+} ions, which must be reduced to Fe^{2+} before titration. The most convenient reducing agent for this purpose is metallic zinc, which reacts with Fe^{3+} ions as follows:

$$2Fe^{3+} + Zn = 2Fe^{2+} + Zn^{2+}$$

Excess metal is removed by filteration through cotton-wool.

Reactions. $K_2Cr_2O_7 + 6FeCl_2 + 14HCl \rightarrow 2CrCl_3 + 2KCl + 6FeCl_3 + 7H_2O$

Ionically : $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

Indicator: A 1% solution of diphenylamine in conc. H_2SO_4 (sp. gr. 1.84).

End point. Appearance of a blue-violet colour ($K_2Cr_2O_7$ solution in the burette).

Procedure. (1) *Preparation of standard $K_2Cr_2O_7$ solution.* Despite the convenience of using solutions of definite normality, the so-called empirical solutions are often used in industrial laboratories. The concentration of an empirical solution does not depend in some simple manner on the gram-equivalent but is determined by various practical considerations and is usually expressed in terms of "titre for the substance determined."

It is more convenient to choose the concentration of the working solution so that the volume taken for the reaction (with a given weight of the substance being analysed) gives the percentage content of the substance or element required in the sample. Thus, the use of empirical solutions in repeated analyses offers great advantage. For the present investigations, let us prepare an empirical $K_2Cr_2O_7$ solution of a concentration such that 1 ml correspond to exactly 0.0025 *g* Fe. To calculate the weight required of $K_2Cr_2O_7$ for preparation of 250 ml of this solution, we know that one litre of the $K_2Cr_2O_7$ solution must correspond to $0.0025 \times 1000 = 2.5$ *g* Fe, and 250 ml to 0.6250 *g* Fe.

By law of equivalence:

One gram-equivalent of $K_2Cr_2O_7$ (49.03 *g*) is equivalent to one gram-equivalent of iron (55.85 *g*).

$$\therefore 0.6250\ g \text{ Fe is equivalent to } = \frac{0.6250 \times 49.03}{55.85} = 0.5488\ g.$$

Hence, weigh out exactly 0.5488 *g* of the $K_2Cr_2O_7$ on an analytical balance and transfer it quantitatively into 250ml measuring flask; dissolve in water, make upto the mark, and mix thorougly. The iron titre of this solution is

$T\ K_2Cr_2O_7/Fe = 0.0025\ g/ml.$

Note. If weighing is done by difference method and exactly 0.5488 *g* $K_2Cr_2O_7$ is not taken, then use actual weight transferred to the measuring flask for calculating the value $T_{K_2Cr_2O_7}/Fe$ and use this value in the subsequent calculation.

(2) *Preparation of the ore-solution.* Weigh out accurately 0.1 *g* of

finely ground air dried ore on a watch glass. Transfer it carefully into a 100 ml flask through a dry funnel, and then weigh the watch glass with the residual ore again. Add about 10-15ml. of conc HCl, washing the ore grains completely with it from the funnel. Warm the flask gently on a sand bath until the dark grains of ore on the bottom of the flask have disappeared and only a whitish silica precipitate remains. The boiling of the contents should be avoided, which may lead to partial volatilization of $FeCl_3$.

(3) *Reduction of Fe^{3+} to Fe^{2+} in the ore-solution.* After dissolving the ore completely, the next step is to reduce the Fe^{3+} ions to Fe^{2+} ions. For this, tilt the flask containing the solution and introduce carefully several pieces of granulated pure zinc metal. Insert a funnel in the neck of the flask to retain splashes and boil the solution until the yellow colour has disappeared. The disappearance of the yellow colour confirms the complete reduction of Fe^{3+} ions to Fe^{2+} ions. This may further be tested by spot test with NH_4CNS solution. Only Fe^{3+} ions give blood-red colour with NH_4CNS.

The solution is, now cooled under the tap and the funnel is removed after washing the drops of liquid from the funnel into the flask. The pieces of unreacted zinc are removed by filtering the solution through cotton-wool, held loosely into the funnel. The small flask, funnel and cotton-wool are thoroughly washed with distilled water and the filtrate is diluted to 300-400 ml. This is done so that the chromic salt formed by the reaction,

$$K_2Cr_2O_7 + 6FeCl_2 + 14HCl \rightarrow 2CrCl_3 + 2KCl + 6FeCl_3 + 7H_2O$$

interfere as little as possible its green colour with determination of the equivalence point in the titration.

(4) *Titration.* The solution obtained in the step (3) is now titrated against $K_2Cr_2O_7$ solution using diphenylamine as the internal indicator. As was explained in detail under redox indicators, the titration must be performed in the presence of H_3PO_4. Further, the acidity of the solution must be fairly high. To satisfy this condition add 25 ml of a mixture of sulphuric acid and phosphoric acid to the solution. To prepare the acid mixture, dissolve 150 ml of H_2SO_4 (sp. gr. $>$ 1.84) in 500 ml of distilled water. When the solution is cool, add 150 ml of orthophosphoric acid, H_3PO_4 (sp. gr. $>$ 1.70) and dilute the mixture with water to one litre. Add one or two drops of diphenylamine indicator solution and titrate the solution with the $K_2Cr_2O_7$ solution, adding the latter in small portions, until a persistent blue-violet colour appears. At first the colour which appears near the end of

the titration disappears fairly rapidly owing to the interaction of the oxidized form of the indicator, formed in the presence of local excess of $K_2Cr_2O_7$, with the Fe^{2+} ions still present in solution.

Therefore, a completely stable colouring of the solution must be aimed at.

Note. The amount of diphenylamine must not be taken more than two drops because at higher concentration with insufficient acidity, and also during very slow titration, the indicator undergoes a different type of chemical change which results (in the presence of excess $K_2Cr_2O_7$) in a green colour instead of blue-violet. If this is the case, reject the titration and repeat.

Calculations. Multiply the number of millilitres of $K_2Cr_2O_7$ solution taken in the titration by its iron titre, and so find the amount of iron in the sample. Then calculate the percentage of iron in the ore.

Exercise 2.11. *Determine the strength of given Mohr's salt solution in grams per litre. You are provided with potassium dichromate solution* $\left(\frac{N}{10}\right)$.

Principle. Ferrous ion when titrated in the presence of hydrochloric acid or sulphuric acid using diphenylamine as an indicator the colour change is not sharp and occurs too easily. This is because the indicator is partially oxidised before the end point is actually reached.

However, a sharp colour change is produced at the end point if phosphoric acid is added to the solution. Phosphoric acid lowers the oxidation-potential of the ferric-ferrous system by forming a complex $[Fe(HPO_4)]^+$ with ferric ions. The chemical reaction can be written as follows:

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3(O)$$

$$[2FeSO_4 + H_2SO_4 + (O) \rightarrow Fe_2(SO_4)_3 + H_2O] \times 3$$

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_4O$$

Ionic Reaction.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$[Fe^{2+} \rightarrow Fe^{3+} + e^-] \times 6$$

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Procedure. Pipette out 10 ml. of the given Mohr salt (Ferrous ammonium sulphate) solution in a clean conical flask. Add 10 ml. of dil sulphuric acid and 2-3 drops of diphenylamine indicator and 2-3 ml. of 1:1 phosphoric acid. The solution is titrated by potassium dichromate solution from the burette with constant shaking until the solution acquires violet-blue coloration on the addition of one drop excess of potassium dichromate solution. Titration is repeated till two or three concordant readings are obtained. Record the observations.

Method of calculation. Let N_1 be the normality of Mohr salt solution and V_2 be the volume of potassium dichromate required for oxidising 10 ml. of the Mohr salt solution.

$$N_1 \times 10 = 0.1 \times V_2$$

or
$$N_1 = \frac{0.1 \times V_2}{10} = 0.01 V_2$$

Hence the strength of the given Mohr. salt (ferrous ammonium sulphate) solution $=$ Normality × Eq. Wt.

$$= 0.01 V_2 \times 392 \ g/l.$$

Determination of the Oxidising Power of Pyrolusite

Pyrolusite when pure consists of manganese dioxide. Its value as an oxidising agent depends upon the percentage of MnO_2 in the sample. This percentage is usually determined by the indirect method in which the manganese dioxide is reduced and dissolved by an excess of ferrous sulphate or oxalic acid in the presence of sulphuric acid and the unused excess determined by titration with standard permanganate solution. The method can also be applied to several other oxidising agents for example to the very similar PbO_2 and to Pb_2O_3 ($= PbO_2 . PbO$) and Pb_3O_4 ($= PbO_2 . 2PbO$).

Procedure.—Grind the mineral in an agate mortar until no grit whatever can be detected under the pestle (Note 1). Weigh out accurately two portions of about 0·5 gram each into 400 ml beakers. Calculate in each case the weight of oxalic acid or sodium oxalate theoretically required to react with the weights of pyrolusite taken.

$$MnO_2 + C_2O_4^{2-} + 4\,H^+ \rightarrow Mn^{2+} + 2\,CO_2 + 2\,H_2O$$

Notes—1. The success of the analysis is largely dependent upon th fineness of the powdered mineral. If properly ground, solution should be complete in fifteen minutes or less.

2. A moderate excess of oxalic acid above that required to react with the pyrolusite is necessary to promote solution; otherwise the residual quantity of oxalic acid would be so small that the last particles of the mineral would scarcely dissolve. It is also desirable that a sufficient excess of the acid should be present to react with a considerable volume of the permanganate solution during the titration, thus increasing the accuracy of the process. On the other hand, the excess of oxalic acid should not be

Weigh out 0·2 gram in excess of this quantity of pure oxalic acid or sodium oxalate into the corresponding beakers, weighing accurately and record the weight. Pour into each beaker 25 ml of water and 50 ml of 6 N sulphuric acid. Cover and warm the beaker and its contents gently until the evolution of Carbon dioxide ceases (Note 3). If a residue remains which is sufficiently colored to obscure the end reaction of the permanganate, it must be removed by filtration.

Finally dilute the solution to 200-300 ml, heat the solution to a temperature just below the boiling, add 15 ml of a manganese sulphate solution and while hot, titrate the excess of oxalic acid with standard permanganate solution (Note 4). From the data obtained calculate the percentage of MnO_2 in pyrolusite.

Iodine. Iodine can also be employed in oxidation-reduction titrations, because the reaction,

$$I_2 + 2e^- \rightarrow 2I^-$$

is reversible. Substance having an oxidation potential much lower than that of the iodine-iodide system are oxidised by iodine. Such

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so large as to react with more of the permanganate solution than is contained in a 50 ml. buret. If the pyrolusite under examination is known to be of high grade, say 80 per cent pure, or above, the calculation of the oxalic acid needed may be based upon an assumption that the mineral is all MnO_2. If the quality of the mineral is unknown, it is better to weigh out three portions instead of two and to add to one of these the amount of oxalic prescribed, assuming complete purity of the mineral. Then run in the permanganate solution from a pipet or buret to determine roughly the amount required. If the volume exceeds the contents of a buret, the amount of oxalic acid added to the other two portions is reduced accordingly.

3. Care should be taken that the sides of the beaker are not overheated, as oxalic acid would be decomposed by heat alone if crystalization should occur on the sides of the vessel. Strong sulfuric acid also decomposes the oxalic acid. The dilute acid should, therefore, be prepared before it is poured into the beaker.

4. Ferrous ammonium sulfate, ferrous sulfate, or iron wire may be substituted for the oxalic acid. The reaction is then the following :

$$2FeSO_4 + MnO_2 + 2H_2SO_4 \rightarrow Fe(SO_4)_3 + MnSO_4 + 2\ H_2O$$

$$\text{or } 2Fe^{++} + MnO_2 + 4H^+ \rightarrow 2\ Fe^{+++} + Mn^{++} + 2H_2O.$$

The excess of ferrous iron may also be determined by titration with potassium bichromate, if desired. Care is required to prevent the oxidation of the iron by the air, if ferrous salts are employed.

substance can be titrated with a standard solution of iodine and is known as Iodimetry.

On the other hand iodide exerts a reducing action upon strongly oxidising systems, thus resulting in the formation of an equivalent amount of iodine. The iodine thus liberated in chemical reactions is titrated with standard sodium thiosulphate solution. This is referred to as Iodometry.

Iodine is a primary standard. It can not be weighed directly on the balance because it is highly volatile. The weighing of iodine is usually carried out in some form of weighing bottle containing potassium iodide. The solution of iodine in potassium iodide has lower vapur pressure and the volatility is thus lowered. The equivalent weight of iodine is one-half of its molecular weight, i.e., 126.91.

Commercial iodine is generally not sufficiently pure to permit of its use as a standard for thiosulphate solutions or the direct preparation of a standard solution of iodine. Besides moisture it may also contain some iodine chloride. It is mixed with potassium iodide and is subjected to sublimation when pure iodine is obtained.

The reason for the wider application of iodine method in volumetric analysis is the accuracy with which a very small concentration of iodine can be detected either by its own colour or by the blue colour produced by the starch indicator or by the red purple colour of iodine when extracted into carbon tetrachloride or chloroform. However, there are two common sources of error in iodometric titration methods.

(1) Iodine is somewhat volatile in solution. This source of error is minimised by the presence of a considerable amount of potassium iodide in the solution which forms a tri-iodide complex $I_2 + I^- \rightleftharpoons I_3^-$. Iodine titrations should not be carried out in hot solution because this would increase volatility loss of iodine.

(2) Iodide gets oxidised by oxygen of the air according to the following reaction,

eaure

$$4I^- + O_2 + 4H^+ \rightarrow 2H_2O + 2I_2$$

The oxidation is fast in acidic solutions as it will contain more hydrogen ions which in turn play a key role in the above reaction. Atmospheric oxidation of iodide is accelerated by strong light and certain catalysts like nitrite, copper and oxides of nitrogen. It is for this reason that the water used in preparing potassium iodide solution should be boiled before use to remove the dissolved oxygen.

For getting better results in Iodometric titrations following conditions must be observed.

(1) Since iodine is volatile the titrations must be carried out in the cold. This is also desirable because the sensitivity of the starch as indicator also decreases with the rise in temperature.

(2) Iodometric titrations should not be performed in strongly alkaline solutions. This is because iodine reacts with alkalies in accordance with the equation,

$$I_2 + 2OH^- \rightarrow IO^- + I^- + H_2O$$

The hypoiodide (IO^- ions) is inadmissible because it is a stronger oxidant than I_2 and partially oxidises thiosulphate to sulphate as follows:

$$S_2O_3^{2-} + 4IO^- + 2OH^- \rightarrow 4I^- + 2SO_4^{2-} + H_2O$$

Higher the hydroxyl ion concentration more thiosulphate will be converted into sulphate. The pH of the solution should not be greater than 9.

(3) Since the solubility of iodine in water is low, excess of potassium iodide must be added in iodometric titrations. The iodine liberated in the reaction then dissolves in potassium iodide forming the complex KI_3. The complexe will release iodine slowly during titration.

(4) As the rate of reaction between the oxidant and I^- is usually too low. Therefore, the solution should be allowed to stand for 2-3 minutes after the addition of the oxidant before the liberated iodine is titrated.

Preparation of 0.1N sodium thiosulphate. It is not possible to prepare sodium thiosulphate solution of definite strength by weighing the pure substance. This is because $Na_2S_2O_3.5H_2O$ effloresces very easily and much a product is not likely to contain exact number of water molecules. An approximate 0.1N solution of sodium thiosulphate is prepared by dissolving 25 gm of A.R. crystallized sodium thiosulphate in double distilled water and the solution is diluted to 1 litre. Keep the solution in a dark place and if it is tobeept for a long time add 3-4 drops of chloroform while the solution is being prepared. Sodium thiosulphate solution can be standardised using standard potassium dichromate solution.

Sodium thiosulphate is a strong reducing agent and the following reaction occurs in the solution,

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$$

Since two moles of sodium thiosulphate liberate two electrons the equivalent weight of sodium thiosulphate is the same as its molecular weight, i.e., 248.19.

Starch indicator. Though iodine itself can be used as indicator because it has intense yellow to brown colour and even a drop of 0.1N iodine imparts a pale yellow colour to 100ml of water. However, a more pronounced colour change can be obtained at the end point if starch is used as an indicator. It reacts with iodine in presence of iodide to form an intensely blue coloured absorption complex which is visible even at very low concentrations. The sensitivity of the starch solution decreases with the increase in the temperature of the solution. Larger concentrations of ethyl and methyl alcohol also decrease the sensitivity of the starch solution. The starch solution should always be freshly prepared. The stock solution of starch can be prepared by adding small amounts of mercuric iodide to the solution. For preparing the starch solution mix 1gm of finely powered solid with 1 ml of ethyl alcohol and 100 ml of water. Boil the solution for few minutes with vigorous stirring till the solution is clear. Cool and keep in a glass stoppred bottle.

Exercise 2.12. *Determine the strength of given solution of potassium dichromate. You are provided with 0.1N sodium thiosulphate solution.*

Principle Potassium dichromate oxidises iodide to iodine in the acidic medium according to the reaction,

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

This reaction is subjected to a number of errors. (1) Hydroiodic acid is readily oxidised by air especially in the presence of Cr^{3+} ions. (2) The reaction is not instantaneous. Therefore, during the titration some solid sodium bicarbonate is added to the acid solution. The solution is allowed to stand for five minutes for reaction to be completed. Titration in good light and against a white background gives a very sharp end point.

Procedure. Take 10ml of the given solution of potassium dichromate solution in a conical flask add to this 10 ml of 10 per cent potassium iodide solution and about 0.5 gm of sodium bicarbonate. Dilute this with about 30ml of distilled water. Allow the solution to stand for about 5minutes so that iodine gets liberated. Rinse and fill the burette with the sodium thiosulphate solution.

Titrate the liberated iodine with sodium thiosulphate solution contained in the burette with constant stirring and when the solution acquires greenish yellow colour add 2.0ml of starch solution. Continue the addition of the thiosulphate solution dropwise till a light green colour is formed. Repeat the titration till concordant values are obtained.

Method of calculation. Let N_1 be the normality of the potassium dichromate solution and V_2 be the volume of 0.1N sodium thiosulphate solution required for reacting with the iodine liberated by 10 ml of $K_2Cr_2O_7$ solution.

$$N_1 \times 10 = 0.1N \times V_2$$
$$N_1 = 0.01 \times V_2$$

Hence, the strength of potassium dichromate solution

$$= 0.01 \times V_2 \times \text{Eq. Wt.}$$
$$= 0.01 V_2 \times 49 \ g/l.$$

Exercise 2.13. *Determine the strength of $CuSO_4.5H_2O$ in grams per litre of the given solution iodometrically. You are provided with 0.1N sodium thiosulphate solution.*

Principle. Iodometric determination of copper is based on the following reaction,

$$2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$$
$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

This shows that Cu^{++} ion gains an electron from the I^- ions and is reduced to Cu^+ ion which is then precipitated as cuperous iodide. Therefore, the equivalent weight of copper sulphate will be the same as its molecular weight, i.e., 249.70 gms. Excess of KI is added to prevent the absorption of iodine on cuperous iodide. Ammonium thiocyanate is added towards the end of the titration which converts cuprous iodide into less soluble cuprous thiocyanate. This has less tendency to absorb iodine, the end point can thus be easily detected.

Procedure. Take 10 ml of copper sulphate solution in a conical flask. Add sodium carbonate solution dropwise till a blue turbidity persists. Dissolve this by adding dilute acetic acid dropwise. This step is done to neutralize the mineral acid present if any. Add 10ml of 10 percent KI solution and stir the solution. Sodium thiosulphate solution is added from the burette in small lots with shaking till the colour of the solution becomes light yellow. Now add 2 ml of starch solution and about 1 gm of solid ammonium thiocyanate. Continue the addition of thiosulphate solution dropwise till the blue colour of the starch iodide disappears. This is repeated till three concordant readings are obtained and record the observations.

Method of calculation. Let N_1 be the normality of the given copper sulphate solution and V_2 be the volume of sodium thiosulphate used for titrating 10ml of $CuSO_4.5H_2O$ solution.

$$N_1 \times 10 = 0.1 \times V_2$$

Normality of copper sulphate solution $N_1 = \frac{0.1 \times V_2}{10}$

Strength of $CuSO_4.5H_2O$ solution $= \frac{0.1 \times V_2}{10} \times 249.5$ *g/l.*

Exercise 2.14. *Determine the amount of available chlorine in the given sample of bleaching powder iodometrically. You are provided with 0.1N sodium thiosulphate solution.*

Principle. Bleaching powder is a mixture of calcium hypochloride $Ca(OCl)_2$ and the basic chloride $CaCl_2.Ca(OH)_2.H_2O$. In addition to this salt some free slaked lime is usually present. The available chlorine in bleaching powder refers to the amount of chlorine liberated by action of dilute acids on bleaching powder according to the following equation,

$$OCl^- + Cl^- + 2H^+ = Cl_2 + H_2O$$

The available chlorine is a measure of the quality of bleaching powder and is expressed as the percentage by weight of the bleaching powder.

The bleaching powder solution or suspension is treated with an excess of a solution of potassium iodide and acidified with acetic acid. The iodine thus liberated is titrated with sodium thiosulphate solution in presence of starch. The chemical reaction can be symbolised as

$$OCl^- + 2I^- + 2H^+ = Cl^- + I_2 + H_2O$$

$$2S_2O_3^{2-} + I_2 = S_4O_6^{2-} + 2I^-$$

Procedure. Weigh out accurately 1.0gram of bleaching powder in a stoppered bottle. Crush the sample thoroughly with requisite portions of distilled water in a mortar until it is disintegrated and no lumps remain. Transfer this to 250ml volumetric flask and dilute, it up to the mark with water.

Pipette out 25.0ml of this solution in a conical flask. To this 10ml of a 10 per cent solution of potassium iodide and 10ml of dil H_2SO_4 are added. Wait for 5 minutes when iodine is liberated. Now add sodium thiosulphate solution from the burette in small amount with constant stirring and continue the addition till the starch solution acquires a pale yellow colour. Add 2ml of starch solution and continue the titration until the blue colour just disappears. The volume of sodium thiosulphate used in the titration is noted and the observations are recorded. This is repeated till two or three concordant readings are obtained.

Method of calculation. Let the weight of bleaching powder dissolved in 250ml = Wg

Strength of bleaching powder $= 4\ W\ g/l$.

Let V_2 ml be the volume of 0.1N sodium thiosulphate solution required for 25ml of bleaching powder solution and N_1 be the normality of the iodine liberated by the bleaching powder.

$$25 \times N_1 = V_2 \times 0.1$$

$$N_1 = \frac{0.1\ V_2}{25}$$

Normality of iodine N_1 = Normality of available chlorine

$$N_{\text{available chlorine}}$$

$$N_{\text{available chloride}} = \frac{0.1\ V_2}{25}$$

$$\text{Strength of available chloride} = \frac{0.1}{25} V_2 \times 35.5\ g/l.$$

Hence, the percentage of available chloride

$$= \frac{0.1 \times V_2 \times 35.5}{25} \times \frac{100}{4W}$$

$$= \frac{3.55 V_2}{W}.$$

2.4.3. Precipitation titrations

Titrations involving precipitation reactions are not nearly so numerous in volumetric analysis as those involving acid-base or redox reactions. Such titrations are usually limited to those involving precipitation of silver ion with anions such as halogens and thiocyanate. The reasons for the limited use of such reactions are: (*a*) Lack of suitable indicator, (*b*) the composition of the precipitate is frequently not known because of co-precipitation effects. Our discussions here will be limited to precipitation titrations involving silver salts with particular emphasis on the indicators which have been successfully employed in such titrations.

It is solubility product which plays a key role in these titrations. For a precipitate of silver chloride the equilibrium constant of the reaction.

$$\text{AgCl(s)} \rightarrow \text{Ag}^+\text{(aq.)} + \text{Cl}^-\text{(aq.)}$$

is
$$\text{K} = \frac{[\text{Ag}^+]\,[\text{Cl}^-]}{[\text{AgCl}]}.$$

The activity of soild AgCl is constant, which by convention may be taken as one. As the solid is sparingly soluble, hence the concentration of Ag^+ and Cl^- ions are small and unless large concentrations of other ions are present, activities can be approximated by molarities, giving.

$$K_{sp}=[Ag^+][Cl^-]$$

The constant K_{sp} is called the solubility-product constant. The precipitation occurs only when the actual ionic product exceeds the solubility product. For a successful application of volumetric analysis the following conditions must be satisfied.

(*a*) The precipitate must be practically insoluble,

(*b*) The formation of the precipitate must be rapid,

(*c*) The titration results should not be distorted appreciably by adsorption (co-precipitation) effects.

(*d*) It must be possible to detect the equivalence point during the titration.

Indicators for precipitation titrations involving silver. The most usual indicators in argentometric titrations are potassium chromate (K_2CrO_4) solution (Mohr's method) or ferric ammonium alum [$NH_4Fe(SO_4)_2$] solution (Volhard's method).

The use of K_2CrO_4 as indicator is based on the formation of Ag_2CrO_4 (brick-red precipitate) by the action of CrO_4^{2-} on Ag^+. The precipitate of Ag_2CrO_4 is produced only after the complete precipitation of Cl^- as AgCl. This is due to the difference between the solubility products of AgCl and Ag_2CrO_4, which are 1.1×10^{-12} and 1.05×10^{-5} *g* ion/l respectively. Therefore, the solubility product of AgCl is reached earlier at a lower concentration of Ag^+ ions than that of Ag_2CrO_4. Consequently, AgCl must be precipitated first. At equivalence point Ag_2CrO_4 begins to be precipitated together with AgCl, and the precipitate suspended in the liquid acquires a red brown colour. This is taken as the end point.

The concentration of the chromate employed as indicator is normally 0.005 to 0.01M.

The Mohr's method is limited to solutions with pH values about 6 to 10. In more alkaline solutions silver precipitates as silver oxide and in acid solutions the chromate concentration is greatly decreased, which makes it necessary to add a large excess of silver ions to bring about the precipitation of silver chromate, and thus leads to a large error. Further this method can not be used for the estimation of iodides (and some bromides) because the colour of the indicator is masked by that of the precipitate and hence, the end point is not easily detectable.

The Volhard's method is based on the precipitation of silver thiocyanate in nitric acid solution, with ferric ion employed to detect excess of thiocyanate

$$Ag^+ + SCN^- \rightarrow AgSCN$$
$$Fe^{3+} + SCN \rightarrow FeSCN^{2+} \text{ (red)}$$

This method is widely used for silver and chloride because of the fact that titration can be performed in acid solution. The acid media is desired to prevent the hydrolysis of indicator, i.e., ferric ion.

In the determination of bromides and iodides by the indirect volhard method, the reaction with thiocyanate does not cause any trouble, because silver bromide has about the same solubility as silver thiocyanate and the silver iodide is considerably less soluble.

Exercise 2.15. *Eastimate the strength of the given NaCl solution by the Mohr's method; provided* $\sim N/30$ $AgNO_3$ *solution.*

Reactions. $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$

Ionically. $Ag^+ + Cl^- \rightarrow AgCl$

Indicator. 2-5 per cent potassium chromate solution.

End point. Appearance if permanent reddish tinge. ($AgNO_3$ solution in the burette)

Procedure (*i*) *Preparation of standard solution of NaCl.* Prepare a standard solution (N/30) of sodium chloride by the method of difference in 250ml measuring flask (Eq. Wt. of NaCl = 58.5)

(*ii*) *Standaradization of* $AgNO_3$ *solution.* Pipette out 20ml of NaCl solution (self-prepared) into a titration flask and add 4-5 drops of potassium chromate indicator. Run in silver nitrate solution gradually with stirring till the precipitate aquires a light reddish tinge. Repeat the titration to get three concordant readings Let the volume of silver nitrate used be V_1 ml.

(*iii*) *Standaradization of given NaCl solution.* Pipette out 20ml of the given NaCl solution and titrate it against $AgNO_3$ solution by using potassium chromate indicator till a reddish tinge is obtained. Repeated the titrations to get concordant readings let it be V_2 ml.

Observations. Record the observations as given in acid-base titrations.

Calculations. Let the Wt. of NaCl taken in 250ml standard solution be $= x\ g$

Normality of standard NaCl solution

$$= \frac{4x}{58.5}$$

$$\text{Normality of } AgNO_3 \text{ solution} = N_{AgNO_3} = \frac{4 \times x}{58.5} \times \frac{20}{V_1}$$

Normality of given NaCl solution

$$N_{\text{NaCl}}=\frac{N_{\text{AgNO}_3}\times V_{\text{AgNO}_3}}{V_{\text{NaCl}}}=\frac{4x}{58.5}\times\frac{20}{V_1}\times\frac{V_2}{20}$$

Strength of NaCl = Normality × Eq. Wt.

$$=\frac{4x}{58.5}\times\frac{V_2}{V_1}\times 58.5=\frac{4xV_2}{V_1}g/l.$$

Exercise 2.16. *Determine the percentage of NaCl and KCl in a mixture of both using Mohr's method provided N/30 $AgNO_3$ solution.*

Reactions. $AgNO_3+KCl\rightarrow AgCl+KNO_3$

$AgNO_3+NaCl\rightarrow AgCl+NaNO_3$

Ionically. $Cl^-+Ag^+\rightarrow AgCl$

Indicator. Potassium chromate solution.

End point. Appearance of Reddish tinge ($AgNO_3$ solution in the burette).

Procedure. (*i*) Prepare a solution of mixture by dissolving an accurately weighed quantity of it, in 250 ml measuring flask. Let it be *x*g.

(*ii*) Titrate it against given $AgNO_3$ solution by taking 20ml in titration flask and adding potassium chromate as indicator. Record the observations as described earlier.

Calculations. Let *V* be the volume of *N*/30 $AgNO_3$ needed for reacting with 20ml of mixture.

$$N_{\text{Mixture}}=\frac{N_{\text{AgNO}_3}\times V_{\text{AgNO}_3}}{V_{\text{mixture}}}=\frac{1}{30}\times\frac{V}{20}=\frac{V}{600}.$$

Let the amount of NaCl present in 250ml be *y* g than strength of NaCl is $=4\times y$......... *g*/*l*

$$\text{Normality}=N_{\text{NaCl}}=\frac{\text{Strength}}{\text{Eq. Wt.}}=\frac{4y}{58.5}\qquad\ldots(i)$$

Similarly Normality of KCl.

$$N_{\text{KCl}}=\frac{4(x-y)}{74.5}\qquad\ldots(ii)$$

Also, Normality of mixture = Nomality of KCl + Normality of NaCl

$$N_{\text{mix}}=N_{\text{NaCl}}+N_{\text{KCl}}$$

$$\frac{V}{600}=\frac{4y}{58.5}+\frac{4(x-y)}{74.5}$$

Knowing *x* and *V*, '*y*' can be calculated

$$\text{Percent of NaCl}=\frac{y}{x}\times 100$$

$$\text{Percent of KCl}=\frac{x-y}{x}\times 100$$

Exercise 2.17. *Determine the amount of $AgNO_3$ dissolved per litre of the given solution by titrating it against ammonium thiocyanate solution ($\simeq N/20$).*

Reactions. $Ag^+ + CNS^- \rightarrow \underset{\text{(white ppt)}}{AgCNS}$

$Fe^{3+} + CNS^- \rightarrow \underset{\text{(Red)}}{[Fe(CNS)]^{2+}}$

Indicator. Ferric alum solution.

End Point. Appearance of red colour (Ammonium thiocyanate in the burette).

Procedure. Prepare a standard solution of silver nitrate (N/20) by dissolving a requisite amount of $AgNO_3$ in distilled water, in 250ml measuring flask (Eq. wt. of $AgNO_3 = 170$)

The exact normality of this solution can be calculated from the amount weighed.

Titrate this solution against ammonium thiocyanate solution taken in burette till a reddish tinge is produced in the supernatant clear liquid. Record this reading. Then titrate the given $AgNO_3$ solution against NH_4CNS solution using Fe^{3+} indicator.

Observations. Record the observations as given in earlier exercises.

Calculation. *Step I.* Calculate the normality of self-prepared $AgNO_3$.

Step II. Calculate the normality of ammonium thiocyanate.

Step III. Calculate the normality of given silver nitrate and multiply this by 170 (Eq.wt.) to get the amount of $AgNO_3$ in the given solution.

Exercise 2.18. *Determine the percentage purity of the given sample of KI you are provided with N/20 $AgNO_3$ solution and N/20 potassium thiocyanate solution.*

Theory. A known quantity of KI is dissolved in water and the solution is made upto 250ml. A known volume of this is now treated with excess of known $AgNO_3$ solution. Silver iodide would precipitate out as yellow precipitate. The excess of $AgNO_3$ is then titrated with potassium thiocyanate using ferric alum as indicator.

Reactions. $KI + AgNO_3 \rightarrow \underset{\text{(yellow ppt)}}{AgI} + KNO_3$

$AgNO_3 + KCNS \rightarrow \underset{\text{(white ppt)}}{AgCNS} + KNO_3$

Ionically. $Ag^+ + I^- \rightarrow Ag\ I$

$Ag^+ + CNS^- \rightarrow AgCNS$

Indicator. 1ml of ferric alum solution.

End point. Appearance of faint reddish colour (KCNS solution in the burette).

Procedure. Dissolve nearly 2g of the given KI in 250ml measuring flask by weighing it with a method of difference. Pipette out 20ml of this solution to 100ml titration flask and add about 20ml of the given $AgNO_3$ solution. This results in the formation of yellow precipitate. Warm the solution with 2ml of dil HNO_3 to coagulate the precipitate and add 1ml of ferric alum indicator. Titrate against KCNS solution until a faint brownish red colour is obtained. Repeat the titration to get three concordant readings.

Observations. See earlier exercises.

Calculation. Strength of KI solution $= 4 \times$ amount transferred to 250ml (x)

$$= 4x \text{g/l}$$

Let V_1ml be the volume of KCNS required to react with excess of $AgNO_3$ solution. As the normalities are equal, V_1 ml will also be equal to the volume of excess $AgNO_3$.

Hence, the volume of $AgNO_3$ which has actually reacted with $KI = (20 - V_1)$ ml.

$$\text{Normality of KI, } N\,\text{KI} = \frac{20 - V_1}{200}$$

$$\text{Strength of Potassium iodide} = \frac{(20 - V_1)}{400} \times 166 \text{ g/l}$$

$$\text{Percentage Purity} = \frac{(20 - V_1)}{400} \times 166 \times \frac{100}{4x}$$

where x is the amount of KI transferred to 250ml measuring flask, while preparing a solution of given KI sample.

Determination of Silver in a Coin

Weigh two portions of the coin about 0·5 gram each. Dissolve them in 15 ml of dilute nitric acid and boil until all the nitrous compounds are expelled. Cool the solution, dilute to 50 ml and 5 ml of the indicator and titrate with thiocyanate to the appearance of faint red coloration. From the corrected volume of thiocyanate solution, calculate the percentage of silver in the coin.

DETERMINATION OF CHLORINE IN A CHLORIDE

Procedure.—Weigh out accurately two portions of the chloride of about 0.20 gram each. Dissolve in 200 ml. of hot water and add 5 ml. of dilute nitric acid which has been previously boiled to remove lower oxides of nitrogen. Calculate the weight of silver nitrate required theoretically to precipitate the chloride from the samples, assuming them to consist of pure sodium chloride unless more specific information as to their nature is available. Into separate small beakers weigh out accurately amounts of pure dry silver nitrate crystals about 10 per cent in excess of the amounts calculated. Dissolve in a little water and add slowly to the corresponding solutions of chloride, rinsing out the beakers thoroughly with hot water to remove all of the silver nitrate (Note 1). Keep the solutions warm until the silver chloride has coagulated sufficiently to yield a clear filtrate. Filter off the precipitate (Note 2) and wash with hot water which has been slightly acidified with previously boiled nitric acid. Titrate the silver in the filtrate with standard thiocyanate solution using ferric alum as the indicator. Calculate the percentage of chlorine (Cl) in the chloride sample (Note 3).

Notes—1. It is also feasible to prepare a stock solution of silver nitrate and add it from a pipet of appropriate volume. The value of a pipetful of the silver nitrate solution in terms of the thiocyanate solution is then established by separate titration. The method does away with the necessity of procuring pure silver nitrate crystals but tends to greater waste of silver.

2. Filtration is necessary since silver thiocyanate is more insoluble than silver chloride and the latter would be converted into the former during the titration.

It is possible to dilute the solution containing the suspended precipitate to exactly 500 ml. in a measuring flask, to filter the well-mixed solution through a dry filter, rejecting the first few millilitres of filtrate, and to collect for titration exactly 250 ml. of the filtrate in a measuring flask. The final results must of course be multiplied by two. This methods eliminates the washing of the precipitate.

3, This method is equally applicable to the analysis of bromides, iodides, cyanides, and thioyanates, all of which yield quantitatively insoluble precipitates with silver ions from acid solution. Except in the case of the cyanide it is not necessary to filter the silver salt precipitate. Silver bromide and silver iodide are each more insoluble than silver thiocyanate.

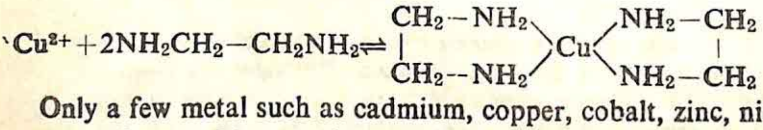
2.4.4. Complexometric Titrations

A complexation titration is one in which a soluble, undissociated, stoichiometric complex is formed at the equivalence point. An example is the reaction of silver ion with cyanide ion to form very stable $Ag(CN)_2^-$ complex.

$Ag^+ + 2CN^- \rightarrow Ag(CN)_2^-$

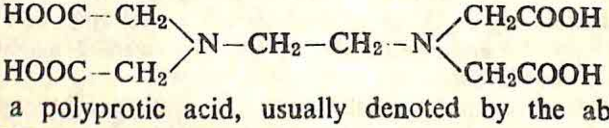
The complexes are formed by the reaction of metal ion, a cation, with an anion or neutral molecule. The metal ion in the complex is called the central atom, and the group attached to the central atom is called ligand and the number of bonds fromed by the central atom is taken as the coordination number of the atom. In the above example, silver is the central atom with coordination number of two, and cyanide is the ligand.

Ligands generally contain an electronegative atom, such as nitrogen, oxygen, or halogen. Ligands having one unshared pair of electrons, such as ammonia (NH_3), are said to be unidentate while ligands having two groups capable of forming two bonds with the central atom are called bidentate. To illustrate—ethylene diamine, with both the nitrogen atoms having unshared electrons, forms complex with cupric ions to show a bidentate character.



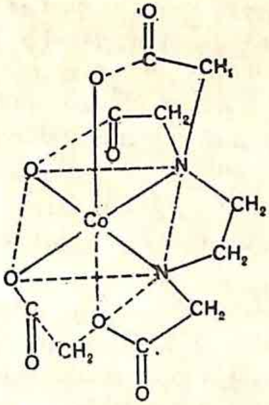
$$Cu^{2+} + 2NH_2CH_2-CH_2NH_2 \rightleftharpoons \begin{array}{l} CH_2-NH_2 \\ | \\ CH_2-NH_2 \end{array} \!\!\!\!\begin{array}{c}\diagdown \\ \diagup\end{array}\! Cu \!\begin{array}{c}\diagup \\ \diagdown\end{array}\!\!\!\! \begin{array}{r} NH_2-CH_2 \\ | \\ NH_2-CH_2 \end{array}$$

Only a few metal such as cadmium, copper, cobalt, zinc, nickel and mercury form stable complexes with nitrogen ligands. Certain other metal ions, e.g., aluminium, lead and bismuth, are better complexed with ligands containing oxygen atoms as electron donors. Certain chelating agents which contain both oxygen and nitrogen are particularly effective in forming stable complexes with a wide variety of metals. A very useful polydentate complexing agent is known as EDTA. This is ethylenediaminetetraacetic acid



$$\begin{array}{l} HOOC-CH_2 \\ \\ HOOC-CH_2 \end{array} \!\!\begin{array}{c}\diagdown \\ \diagup\end{array}\! N-CH_2-CH_2-N \!\begin{array}{c}\diagup \\ \diagdown\end{array}\!\! \begin{array}{l} CH_2COOH \\ \\ CH_2COOH \end{array}$$

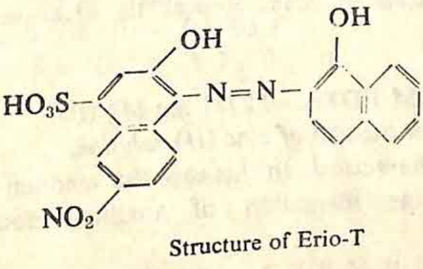
EDTA is a polyprotic acid, usually denoted by the abbreviated formula H_4Y. It is potentially a sexidentate ligand which may coordinate with a metal ion through its two nitrogens and four carboxyl groups. This forms octahedral complexes with metal ions. The structure of EDTA-cobaltous complex is given below:



For convenience, the free acid form of EDTA is often abbreviated H_4Y and the complexes become CoY^{2-}, CuY^{2-}, FeY^{2-} etc.

The generic term for the entire class of reagents that form stable, water soluble, 1:1 complexes with metal ions and which hence may be employed as titrants for metals. is chelon (pronounced as 'Key-loan'). The complexes, a special class of chelates are called metal chelates, and the titrations are termed as chelometric titrations.

Indicators for chelometric titrations. An indicator for EDTA titrations is a compound that forms a less stable complex with the metal ion than the metal-EDTA complex. The indicator releases metal ion at the equivalence point, and changes colour during the titration. A well studied example is Eriochrome Black T (Erio T), an O,O' dihydroxyazo dye having the following structure :



Structure of Erio-T

Metal chelates are formed with this molecule by loss of hydrogen ions from the phenolic OH groups and the formations of bonds between the metal ions and the oxygen atoms as well as the azo group. Erio T is a triprotic acid and is usually abbreviated as H_3E. In acid solution. the indicator is in the form H_2E^-, which is red. Between pH 6.5 and pH 10, the HE^{2-} blue form is present and above pH 10, yellow orange E^{3-} exists. The indicator forms stable 1:1 complexes, which are wine-red in colour, with a number of cations such as Mg^{2+}, Ca^{2+}, Zn^{2+} and Ni^{2+}. Many EDTA titrations are performed in buffers of pH 8 to 10, the range in which the predominant form is the blue HE^{2-}.

Preparation of the standard solution. The dihydrate of the sodium salt $Na_2H_2Y.2H_2O$ (Mol.wt. 372.24) is commonly used in reagent solutions because the acid is quite insoluble in water. The disodium salt dihydrate, is commercially available in high purity, easy to purify, store and use as a primary standard. Stored in glass bottles it is very stable for many months. But the titer may decrease by leaching of metal ions from the glass, if stored in glass containers. For the preparation of 0.1M EDTA solution dissolve 37.22g of dissodium salt of EDTA, stoichiometrically dried product (dried at 80°C for 2-3 days) in one litre of distilled water.

Exercise 2.19. *Determination of magnesium, (II) ions in the given solution ~0.01M Mg (II).*

Theory. The given solution containing Mg (II) can be titrated with EDTA without any difficulty, except that the rate of reaction is slow between the Mg-ErioT complex and EDTA.

Procedure. Pipette out 25ml of Mg (II) solution into a titration flask and dilute it with 25ml of distilled water. Add 5-10ml of buffer (pH = 10, NH_4Cl in NH_4OH.) and 2ml of 10 per cent Erio Black T indicator. Titrate against EDTA solution taken in burette until the colour changes from Red to blue. Repeat the titration to get concordant readings.

Calculation.

1ml 0.01M EDTA = 0.2731 mg Mg (II).

Exercise 2.20. *Standardization of zinc (II) solution.*

Procedure. Same as Exercise 1. In this case the medium should be ammonical to effect the formation of auxiliary complex, zinc tetramine.

Calculation. 1ml of 0.01 M EDTA = 0.5637 mg. Zn (II).

Exercise 2.21. *Determine the amount of calcium and magnesium present in sea-water.*

Obtain a sample of sea-water and record the number. Pipette out 25ml of this solution into 500ml volumetric flask and make up to the mark with distilled water. The diluted solution is used for analysis.

Determination of Ca(II) and Mg(II). Pipette out 25ml into a titration flask and add 5ml of pH 10 buffer, 25ml of distilled water and 2 drops of Erio T indicator. Heat the solution to about 60°C and titrate at this temperature with EDTA solution until a purple colour is obtained. Swirl the flask for 20 seconds, then continue titrating, adding EDTA dropwise with constant shaking until blue colour with no tinge of purple is obtained.

This gives the total Ca (II) and Mg (II) concentration.

Determination of Ca (II). Pipette out 25ml of sea-water sample and dilute with 25ml of distilled water and add 3ml of 50% NaOH. The Mg(II) will precipitate as $Mg(OH)_2$. Shake for two minutes. Rinse down the sides of the flask with little distilled water. Add 2 drops of calcon indicator and titrate with EDTA drop wise until a drop of EDTA turns the solution blue, but the purple will return within 20 seconds. At this stage, allow the solution to stand for 5 minutes with occasional swirling. Some of the calcium is precipitated as $CaCO_3$ and this allows dissolution of $CaCO_3$ to ensure the correct end point. Continue titration to obtain blue colour. This should persist for 20 seconds.

Calculation:

1 ml 0.01M EDTA = 0.4008 mg Ca (II)
1 ml 0.01M EDTA = 0.2731 mg Mg (II)

Let the volume of EDTA consumed in the determination of Mg & Ca both, with Erio T be = X ml. and with Ca (II) only, i.e., with calcon indicator be = Y ml.

Then mg of Ca (II) = 0.4008 *Y*
mg of Mg(II) = (*X*-*Y*). 0.2431

3

Gravimetric Analysis

Gravimetric analysis involves the determination of the amount of some constituent of a given sample by weighing operation. That is, this constitutent is separated from the remainder of the sample and weighed accurately. The object of most gravimetric techniques is in achieving this separation. Often the constituent can be separated by converting it to some other form of known definite composition.

In the most important method of gravimetric analysis, the sample, if solid, is dissolved to prepare a solution of known concentration. The precipitant is chosen to give a precipitate of small solubility and definite known composition. The precipitate obtained is then quantitatively separated from the aqueous phase, dried and then weighed accurately.

In addition to precipitation, other methods are also used. For example, volatile components (H_2O, CO_2, etc.) of a substance are often determined by volatilization, the substance is warmed or ignited and the amount of the component is found from the loss in weight. Thus, the determination is made either by collecting the substance evolved on heating and weighing it, or by determining the weight loss of the original material. Out of the two methods, the precipitation technique is the one most used. The various important steps involved in this technique are discussed below:

(*A*) Precipitation

For a successful precipitation method, one must select, (*a*) the appropriate precipitate from among the various insoluble compounds that can be obtained from the desired constituent, and (*b*) the optimum physical conditions to effect the actual precipitation. The most important factors in making these choices are as follows:

(1) Choosing the precipitate. (*a*) *Completeness and specificity of precipitation*. The precipitated form should have low solubility, *i.e.*, the amount remaining in solution, after filteration should be less than the error of the ordinary analytical balance (0.1mg). This can be conveniently determined by the solubility product principle. The other important factors for complete precipitation are—presence of common ions, dissimilar ions, acids, bases and changes of temperature.

Secondly, the precipitating agent should be selective and specific, i.e. it should precipitate only the substance being analyzed and no other.

(*b*) *Stoichiometry of the precipitate*. It is also desirable that the precipitate must be convertible into a stable pure substance of definite chemical composition and the structure of the precipitate should be such as to allow of rapid filteration and washing. This can be effected either by ignition or simple chemical operation such as evaporation with a suitable liquid. The simple heating of the filtered, washed precipitate to the appropriate temperature is termed as ignition. Ignition helps to remove absorbed water, occluded water, or water of hydration. This may also be used to convert the precipitate to another, analytically more favourable compound.

(2) **Conditions for precipitation**. As already pointed out, the physicial state of the precipitate must be such that it can be easily separated from the solution by filteration and can be washed free of soluble impurities. For this, the particles should be homogeneous, sufficiently large so as not to pass through filtering medium, and the particle size should not change by the washing process.

The mode of precipitation plays a key role in controlling the physical state of the precipitate.

To obtain coarsely crystalline precipitates the following procedures are generally adopted.

(*i*) To increase precipitate solubility and decrease supersaturation, hot solutions are used.

(*ii*) To ensure good initial nucleation, the degree of supersaturation is minimized by adding a dilute solution of precipitant slowly with thorough stirring.

(*iii*) Precipitation from homogeneous solution is the best way of ensuring the small degree of supersaturation that is desired.

(*iv*) To obtain large primary particles a suitable reagent is often added which increases the solubility of the precipitates.

(*v*) Digestion, which is the process of allowing the crystals stand for a long time in contact with the mother liquor, often causes the transformation of small imperfect, and impure crystals into larger, more perfect and purer ones. The basic process occuring in digestion is the recrystallization of the precipitate under more favourable conditions.

Practical means of obtaining a filterable precipitate include digestion, temperature change, stirring or agitation and addition of a suitable electrolytes. When pure water is used for washing, many precipitates are *peptized*, i.e., converted into the colloidal state (because of redispersion of the precipitate by the removal of the adsorbed electrolyte), so that part of the precipitate passes through the filter. To prevent this undesirable effect, i.e., peptization, the precipitate must be washed with a dilute solution of an electrolyte rather than with pure water. The electrolyte must, of course, be a volatile substance which is removed completely from the precipitate by ignition.

The second requirement for a precipitate is that it can be washed free from impurities and particles that make it up should be homogeneous. Inhomogeneity is due to several sources such as, *Simultaneous precipitation*, which occurs when the solubility products of other compounds are exceeded, *Co-precipitation*, which occurs when foreign material is brought down either as surface impurities (this is maximum for gelatinous precipitates), giving *surface adsorption*, or as material occluded during crystal growth, giving occlusion, and post precipitation which occurs when two precipitates are formed, at different rates. By selecting the proper experimental conditions, contamination of the precipitate due to precipitation and post precipitation can be counteracted.

Both occlusion as well as surface adsorption occur during the process of precipitation. Adsorption of ions from the mother liquor over the precipitated particle is known as surface adsorption. This is more in smaller particles. Occlusion, on the other hand, involves the entrapment of impurities within the lattice structure of a crystalline precipitate. Both types of contamination can be reduced by maintaining a low degree of supersaturation during precipitation and by digestion. Surface adsorption is also removed by washing the precipitate.

(*B*) Filtration

In quantitative analysis filtration must be conducted with much greater care than is sometimes given in qualitative analysis. Filtration should be done using gravimetric filter paper of suitable pore size. These papers have a very small ash content. The filter paper used must be of such texture as to retain smallest particles of precipitate and yet permit of rapid filteration. Generally three textures are made, one for very fine precipitates, second for the average precipitate which contains medium-sized particles and a third for gelatinous precipitates and coarse particles.

Whatman filter papers have been found to be very satisfactory for gravimetric work. Three grades of Whatman filter papers of size 9cm and 11cm are commonly employed. No. 42 is used for the finest precipitates but are slow for filtering. No. 40 is used for gelatinous precipitates. No. 41 is used for other common purposes, where No. 42 is slow filtering and No. 40 has large pore size. The funnel with an angle 60 and a stem of length about 15cm should be used in order to promote rapid filtration. Set up the filtration assembly. Start the filtration by decanting liquid into the funnel in order to avoid an immediate build-up of solid particles which can clog the pores of the paper. The stem of the funnel should be vertical with its tip touching the side of the receiving beaker. The liquid is directed to the side of the filter using a glass rod. The last trace of the precipitate is removed from the beaker using a jet of water from a wash bottle.

Precipitate adhering to the beaker may be removed with a rubber tipped rod called 'policeman.'

In case of gelatinous precipitates of $Al(OH)_3$ and $Fe(OH)_3$ which tend to clog the pores of the filter paper, filter pulp is added immediately before filtration.

For more accurate work filter crucibles are also used. Three types of filter crucibles are used, gooch crucible, sintered porcelain and sintered glass crucible. A gooch crucible is made of porcelain and has a perforated base which can be covered with a mat of asbestos to serve as a filter medium.

A sintered porcelain crucible has a porous base. Both these types are suitable for filtering solids which after filteration are heated strongly in the absence of filter paper.

A sintered glass crucible is made of glass and has a porous filter base. Since it can not stand high temperatures required for ignition it is primarily used to filter solids which have to be dried at temperatures in the region of 100°C.

Most precipitates are produced in the presence of one or more soluble compounds. Since the latter are frequently not volatile at the temperature at which the precipitate is ultimately dried. The purpose of washing a precipitate is to remove adsored impurities and the mother liquor which permeates the precipitate. Adsorbed impurities are in equilibrium with the corresponding ions in solution. The minimum volume of the washing liquid required to remove the objectionable matter should be used since no precipitate is absolutely insoluble. The choice of liquid used for washing a particular precipitate is important. When pure water is used for washing many precipitates are peptised. Peptisation is a process in which a precipitate is converted into colloidal state, as a result of this part of the precipitate is lost. The precipitate should, therefore, be washed with a dilute solution of an electrolyte rather than pure water. It is better to wash a precipitate with a number of small portions of the washing liquid than with one or two large portions.

The ideal washing liquid should satisfy the following conditions:

1. It should not have an dispersive action on the precipitate.
2. It should be volatile at the temperature of drying of the precipitate.
3. It should not dissolve the precipitate.
4. It should contain no substance which is likely to interfere with the determination of the precipitate.

Ammonium salts are generally used for washing the precipitate for example ammouium nitrate solution for washing ferric hydroxide.

(*C*) Drying and Ignition of Precipitates

The precipitate after careful washing must be brought to a constant composition before it can be weighed. The further treatment depends upon the nature of the filtering medium and of the precipitate.

Drying is a process in which a precipitate is heated below 250°C. Ignition involves heating the precipitate from 250-1200°C. Drying may be done by keeping the pre-

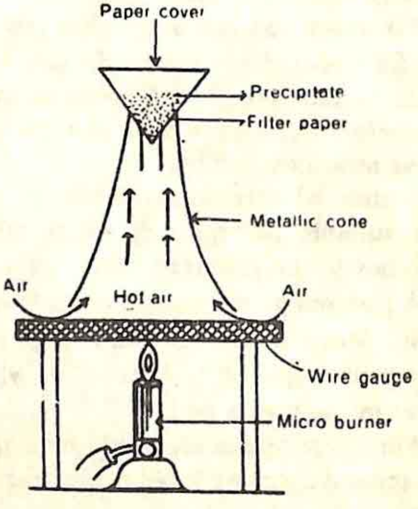


FIG. 3.1 Drying the Precipitate

cipitate in the electric oven, maintained at 150°C.

The conventional method of drying the precipitate consists in placing the funnel containing the precipitate on a cone which is kept on a wire gauge or sand-bath placed on a tripod stand. Heating is done with a burner placed below it. This is shown in Fig. 3.1. The stem of the funnel should not touch the hot sand bath. When drying is complete the filter paper will begin to separate from the funnel. Avoid over-heating the filter paper.

Take a silica or porcelain crucible bring this to constant weight by heating. In case of precipitate like $Fe(OH)_3$, $Al(OH)_3$ etc. which are not attacked by carbon of the filter paper, precipitate is ignited along with the filter paper.

The precipitates such as $BaSO_4$, CuO, ZnO which get reduced by the carbon of the filter paper are heated after separating them from the filter paper. The filter paper is folded so as to completely enclose the precipitate and is placed point down in the weighed crucible which is supported on a clay-pipe triangle. It is slightly inclined as partially covered with the lid as shown in Fig. 3.2. The precipitate first dries

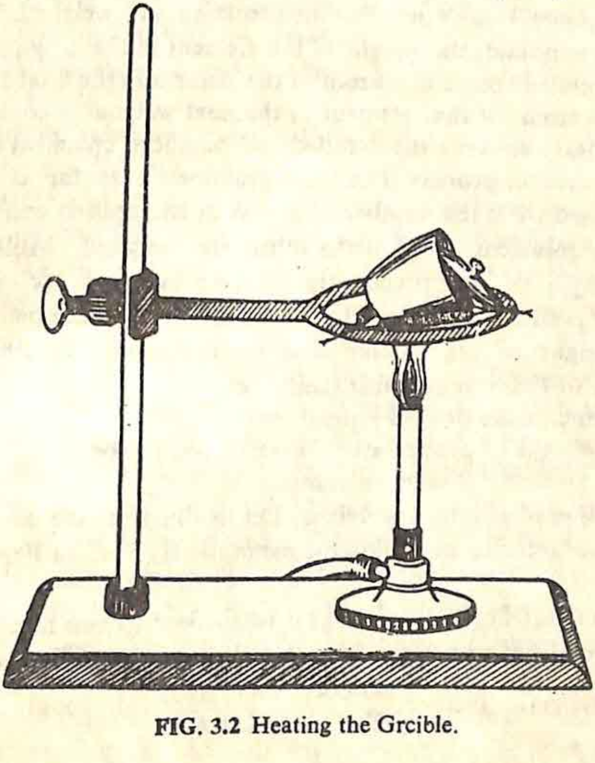


FIG. 3.2 Heating the Grcible.

completely and then chars slowly without catching fire. If the paper catches fire, the burner should be removed and the flame allowed to go out. When the filter paper has charred and smoking has ceased, the burner flame is gradually increased. When all the carbon has burned the crucible is covered completely and kept in a vertical position. The flame is now increased and heating is done for 15-20 minutes to complete the ignition. At the end of ignition the crucible is allowed to cool below redness in the air, and then while it is still hot, it is placed covered in the desiccator.

(*D*) Weighing

The precipitate after drying and ignition is finally weighed. Weighing is, therefore, a very important operation in quantitative analysis and must be done very accurately. For detailed procedure see Chapter 1.

Method of calculation. In the gravimetric determination of an element in a sample, the element can seldom be isolated and weighed directly, instead it is quantitatively converted to a pure compound of definite composition, which is then isolated and weighed. From the weight of compound, the weight of the element in the original sample can be calculated. Since one atom of the element in the final estimation yields one atom of that element in the final weighable compound, it is not necessary to write the detailed and balanced chemical equations for the conversion process. The term gravimetric factor is generally employed which is the number of grams of the desired constituent in 1g (or the equivalent of 1g) of the substance weighed. Multiplication of the weight of the precipitate by the gravimetric factor gives the number of grams of the desired constituent in the sample. Division by the weight of the sample and multiplication by 100 gives the percentage of the desired constituent, i.e.,

Percentage of the desired constituent

$$= \frac{\text{Weight of precipitate} \times \text{gravimetric factor}}{\text{Weight of sample}} \times 100$$

Calculation of gravimetric factor. Let us illustrate the calculation of gravimetric factor in the following examples (*i*) FeO in Fe_2O_3, (*ii*) Cl in AgCl.

(*i*) One mole of Fe_2O_3 (159.691g) is equivalent to two moles of FeO. Two moles of FeO are required to make one mole of Fe_2O_3

The gravimetric factor: $\frac{2FeO}{Fe_2O_3} = \frac{2(71.845)}{159.691} = 0.89981$

(*ii*) One mole of AgCl, (143.32g) contains one mole of Cl atoms (35.453g).

$$\text{The gravimetric factor} = \frac{\text{Cl}}{\text{AgCl}} = \frac{35.453}{143.323} = 0.24736$$

Exercise 3.1. *Estimate the amount of sulphate ions in grams per litre of the given solution.*

Principle. The analysis of a soluble sulphate is based upon precipitation with barium ion. The method consists in slowly adding a dilute solution of barium chloride to a hot solution of the sulphate acidified with dil hydrochloric acid.

$$Ba^{2+} + SO^{2}_{4}{}^{-} \longrightarrow \underset{\text{ppt}}{BaSO_4}$$

The barium sulphate is collected on a suitable filter paper washed with water and strongly ignited. Superficially this method appears straight forward. Infact however, it is subject to a large number of interferences. Some of the interference are the following:

1. Excessive amounts of mineral acid should be avoided. If added it would cause co-precipitation of alkali metals, ammonium and calcium ions result in low results.

2. Iron is co-precipitated as a basic ferrous sulphate, which also lowers the result.

3. Barium sulphate is partially reduced to BaS if filter paper is charred too rapidly.

Purification and reprecipitation is not feasible because there is no practical solvent for barium sulphate. It is therefore necessary to eliminate the main interferences by preliminary treatment of the sample and then to precipitate barium sulphate from hot dilute solutions.

Procedure. Pipette out 20ml of the given solution into a 400ml beaker. Add 10-15 drops of conc. HCl and dilute to 100-150ml with distilled water. Heat the solution to 70°C and to the hot solution add barium chloride solution very slowly with constant stirring until the precipitation is complete. Allow the precipitate to settle and test for complete precipitation by adding a few drops of precipitant. Digest the solution on a water-bath for half an hour. Filter the solution hot using Whatman No 42 filter paper. Wash the precipitate with hot water until the washings are free from chloride ions (Test 4-5 drops of washing with 1 or 2 drops of silver nitrate solution, absence of white turbidity indicates complete removal of chloride ions).

Dry the precipitate on a drying cone. Fold the filter paper and transfer it to a weighed crucible. Cover it partially by lid and heat the crucible with a small flame until the paper chars and volatile matter is expelled. When the charring is complete raise the temperature of the crucible. Ignite the crucible to a triange heat for 10-15 minutes. Cool the crucible and the precipitate. Repeat the ignition for about 10 minutes and take the weight after cooling in a desiccator, until constant weight is obtained. Record the observations. Let *Wg* be the weight of the precipitate of barium sulphate.

Method of calculation.

$$\underset{233.42}{BaSO_4} \rightarrow \underset{96.0}{SO_4^{2-}}$$

233.42 g of Barium sulphate = 96.0 g of SO_4^{2-} ions.

$$= \frac{96.0}{233.42} + W \text{ g of } SO_4^{2-} \text{ ions.}$$

Wg is the weight of $BaSO_4$ obtained from 20ml of the solution. Hence the amount of SO_4^{2-} ions per litre of the given solution:

$$= \frac{96.0 \times W \times 50}{233.42} \text{ g.}$$

Precautions. 1. Precipitation should be carried out from hot dilute solution and the precipitant should be added with constant stirring.

2. The precipitate must be free from chloride ions before drying.

3. The precipitation should be carried out in presence of a mineral acid.

4. Since on heating some $BaSO_4$ is converted into BaS due to reduction by carbon, so addition of one drop of HCl and one drop of H_2SO_4 is necessary.

Result. The amount of sulphate ions per litre of the given solution was found to be = . . . *g*.

Exercise 3.2. *Estimate the amount of Barium ions in grams per litre of the given solution.*

Principle. Barium is precipitated from the solution slightly acidified with HCl by a hot solution of dil H_2SO_4. The details for the experiment are identical with those given in Exercise 3.1.

Calculation.

$$\underset{137.36}{Ba} \equiv \underset{233.42}{BaSO_4} \equiv \underset{244.30}{BaCl_2.2H_2O}$$

Since 233.42*g* Barium sulphate = 137.36*g* of Ba^{++} ions

$$\therefore \quad W \text{ g of } BaSO_4 = \frac{137.36}{233.42} \times W\text{g of } Ba^{++} \text{ ions}$$

W is the weight of $BaSO_4$ obtained from 20ml of the solution. Hence, the amount of Ba^{++} ions per litre of the given solution.

$$=\frac{137.36\times 50\times W}{233.43}\text{ g of barium per litre.}$$

Result. The amount of Ba^{2+} ions in the given solution was found to be . . . *g/l*.

Exercise 3.3. *Estimate the amount of Al^{3+} ions in grams per litre of the given solution gravimetrically.*

Principle: The aluminium is precipitated as hydrated oxide by adding ammonia as precipitant in the presence of ammonium chloride. The gelatinous precipitate of aluminium hydroxide is formed as under:

$$Al^{3+}+3OH^{-}\longrightarrow Al(OH)_3$$

The precipitate is washed and ignited to form aluminium oxide, Al_2O_3

$$2Al(OH)_3\xrightarrow{\text{ignition}}Al_2O_3+H_2O$$

However, this widely used method involves considerable complications in actual practice, these are (*i*) since, $Al(OH)_3$ is an amphoteric hydroxide and is appreciably soluble is excess of ammonium hydroxide. Therefore, for complete precipitation the solution pH must be adjusted very precisely. This is achieved by using methyl red indicator, (*ii*) It is rather difficult to filter off the precipitate and to wash out absorbed impurities. The filtration can be accelerated by adding paper pulp, (*iii*) The weighed form (Al_2O_3) is highly hygrosocopic and special precautions have to be taken when the ignited precipitate is cooled and weighed, (*iv*) Ammonia precipitates number of other cations such Co^{++}, Cu^{++}, Ni^{++}, Zn^{++} etc. (coprecipitation). This can be minimised by precipitating in presence of ammonium chloride which acts as a buffering agent.

Procedure. Pipette out 20ml of the given solution into a 400ml beaker. Add 5g of pure ammonium chloride and a few drops of methyl red indicator. Dilute the solution to 200ml with distilled water. Heat the solution to boiling and add a dilute solution of ammonia (1:1) dropwise with constant stirring. Continue the addition of ammonia until the colour of the solution changes to yellow. Add 2ml of paper pulp and boil the solution for 2-3 minutes. Filter through Whatman No. 40 and wash it with 2 per cent ammonium nitrate solution 3-4 times. Test the washing for the complete removal of sulphate ions with barium chloride solution.

Dry the precipitate on a heating cone. Now fold the filter paper with the precipitate and transfer it to a weighed crucible. First heat with a low flame and when paper is charred increase the flame using

Meker burner for half an hour. Cool the crucible first in air then in a desiccator. Weigh the crucible along with the precipitate accurately. Repeat the process of heating for 10-15 minutes till the weight is constant. Record the observations. Let *Wg* be the weight of aluminium oxide precipitate.

Method of calculation

$$K_2SO_4.Al_2(SO_4)_3.24H_2O \equiv Al_2O_3 \equiv 2Al$$

$$948.85 \qquad\qquad 102 \qquad 54$$

$$102g \text{ of } Al_2O_3 = 54g \text{ of } Al^{3+}$$

$$W \text{ g of } Al_2O_3 = \frac{54}{102} \times W$$

Since W g is the weight of Al_2O_3 obtained from 20.0 ml of the water.

Hence the amount of Al^{3+} ions per litre of the given solution = Gravimetric factor × Weight of precipitate × 50

Precautions. 1. The precipitation should be carried out from hot dilute solution and the precipitant should be added with constant stirring.

2. The precipitate must be free from sulphate ions.

3. Paper pulp should be added to increase the rate of filtration.

4. Wash the precipitate with 1 per cent ammonium nitrate solution to prevent peptization.

Result. The amount of Al^{3+} ions per litre of the given solution was found to be. . . . . *g/l*

Exercise 3.4. *To estimate the amount of nickel (Ni^{2+}) as nickel dimethylglyoxime, in grams per litre.*

Principle. Nickel is quantitatively precipitated by alcoholic solution of dimethylglyoxime from very weakly acid or ammonical solution. It forms a scarlet precipitate having the structure, $Ni\ (C_4H_7O_2N_2)_2$. It is soluble in free mineral acids, alcoholic solutions containing more than 50 per cent alcohol by volume, hot water and concentrated ammonical solutions of cobalt salts. It is insoluble in dilute solutions of ammonia and solutions of ammonium salts.

Iron, aluminium and chromium interfere as these are precipitated as hydroxides on the addition of dimethylglyoxime. This can be prevented by the addition of tartaric acid which will mask these cations.

Procedure. Take 20ml nickel (*II*), salt solution in a 400ml beaker and dilute it by the addition of 100ml of distilled water. Heat the solution upto 70-80°C. Add slight excess of 1 per cent solution of dimethyl glyoxime followed by the addition of dil. ammonia (1:1) dropwise directly to the solution with constant stirring until precipitation takes place and, then, in slight excess. Digest the precipitate on water-bath for half an hour and test the solution for complete precipitation when the precipitate has settled down. Keep the precipitate for one hour, cooling at the same time. Filter the precipitate through sintered glass crucible. Wash the precipitate with cold water until free from chloride ions and dry it, at 110-120°C for 45-50 minutes. Allow to cool in a desiccator and weigh. Repeat the drying until constant weight is attained. Weigh as $Ni(C_4H_7O_2N_2)_2$.

Method of calculation

$$NiCl_2.6H_2O + 2DMG \longrightarrow \underset{\substack{Ni\,(C_4H_7O_2N_2)_2 \\ 288.69}}{[Ni(DMG)_2]}$$

288.7 g of nickel dimethylglyoxime $= 58.7$g of Ni^{++} ions

$$= \frac{58.7}{288.7} \times W \text{ g of } Ni^{++} \text{ ions}$$

W is the weight of nickel dimethylglyoxime from 20ml of the given solution. Hence, the amount of Ni^{++} ions per litre of the given solution

$$= \frac{58.7 \times 50 \times W}{288.7} \text{ g per litre}$$

Precautions. 1. Precipitation should be carried out in hot solution.

2. Precipitation must be complete before filteration.

3. The precipitate should be washed with hot water.

4. The precipitate should dry before weighing and it should be dried at 110-120°C.

Result. The amount of Ni^{2+} ions in g per litre of given solution was found to be. . . . *g/l*.

Exercise 3.5. *To estimate the amount of copper (Cu^{2+}) ions as cupric oxide, in grams per litre.*

Principle. Copper (II) ion forms an insoluble precipitate of copper hydroxide when treated with sodium hydroxide. On heating, the $Cu(OH)_2$ loses water and is converted into copper oxide.

$$CuSO_4 + 2\,NaOH \longrightarrow \underset{ppt.}{Cu(OH)_2} + Na_2SO_4$$

$$Cu(OH)_2 \xrightarrow{heating} CuO + H_2O$$

Procedure. Take 20ml of $CuSO_4.5H_2O$ solution in a 400ml beaker and dilute it up to 120ml with distilled water. Add 1ml conc. HCl and few drops of phenolphthalein. Heat the solution to boiling and add sodium hydroxide solution dropwise till the supernatant liquid in the beaker appears, pink in colour. Boil the solution again for few minutes and then allow the ppt to settle down. Filter the precipitate through Whatman filter paper No. 40 and wash the precipitate 3-4 times with hot water by decantation and then transfer the ppt. on filter paper with the aid of policeman. Wash the ppt. on filter paper until the filterate is free from alkali and sulphate ions (no turbidity with $BaCl_2$).

Now fold the filter paper into a small packet and transfer it in a weighed silica crucible. Ignite the paper carefully in such a way that the ash formed, drops into the crucible. Heat the crucible till all the carbonaceous material has burnt off. Cool the crucible and add 2-3 drops of conc. HNO_3. Heat the crucible gently over a small flame until fumes cease and then heat strongly for half an hour. The function of HNO_3 is to reoxidise cuprous oxide into cupric oxide which is formed by the reduction of carbon. The reaction may be written as given below:

$$2CuO + C \longrightarrow Cu_2O + CO$$

$$Cu_2O + C \longrightarrow 2Cu + CO$$

$$Cu/Cu_2O \xrightarrow{HNO_3} Cu(NO_3)_2$$

$$2Cu(NO_3)_2 \xrightarrow{Heat} 2CuO + 4NO_2 + O_2$$

Cool the crucible first in air and then in desiccator at room temperature, and weigh it. Repeat the process of heating cooling and weighing till a constant weight is obtained.

Method of calculation

$$\underset{63.5}{Cu} \equiv \underset{79.5}{CuO} \equiv \underset{249.7}{CuSO_4.5H_2O}$$

$$79.5g \text{ of copper oxide} = 63.5g \text{ of } Cu^{++} \text{ ions}$$

$$W\,g \text{ of copper oxide} = \frac{63.5}{79.5} \times W$$

$W\,g$ is the weight of CuO obtained from 20ml of given solution. Hence, the amount of Cu^{++} ions per litre of the given solution

$$= \frac{63.3}{79.5} \times 50 \times W\,g$$

Precautions. 1. Precipitation should be carried out in hot dilute solution.

2. Precipitant should be added dropwise and excess of precipitant should be avoided because $Cu(OH)_2$ is slightly soluble in excess of NaOH.

3. Precipitation must be carried out in the presence of HCl otherwise some basic salts may interfere.

4. Do not allow the precipitate to dry and to stick the sides of beaker.

5. Sulphate and Chloride ions must be completely removed before drying the precipitate.

6. Ash must be cooled before treating with conc. HNO_3.

Result. The amount of Cu^{2+} ions per litre of the given solution was found to be. . . . *g/l*.

Exercise. 3.6. *To estimate the amount of Copper, Cu^{2+} ions as cuprous thiocyanate in gms per litre.*

Principle. This is an excellent method, since most thiocyanates of other metals are soluble in water. The addition of 2-3g of hydrochloric acid is desirable for the prevention of hydrolysis when bismuth, antimony or tin are present. Excessive amounts of ammonium salts or of the thiocyanate precipitant should be absent as they are also oxidising agent. The solution should be slightly acidic, since the solubility of CuSCN precipitate increases with decreasing pH. The reaction may be represented as:

$$2Cu^{++} + HSO_3^- + H_2O \longrightarrow 2Cu^+ + HSO_4^- + 2H^+$$

$$Cu^+ + SCN^- \longrightarrow \underset{\text{ppt.}}{CuSCN}$$

The precipitate is curdy and is readily coagulated by boiling.

Procedure. Take 20ml of $CuSO_4.5H_2O$ solution into 400ml beaker. Add a few drops of hydrochloric acid and the a slight excess of freshly prepared saturated sulphurous acid solution. The experiment can also be performed by the addition of 10g sodium bisulphite and 10ml of dil HCl (in place of H_2SO_3). Dilute the solution by addition of 100ml of distilled water. Heat the solution nearly to boiling and add freshly prepared 10 per cent ammonium thiocyanate (ammonium sulphocyanide) solution, slowly with constant stirring. The precipitate of cuprous thiocyanate should be white, the mother liquor should be colourless and give smell of sulphur dioxide. Keep the precipitate overnight. Check the solution for complete precipitation by the addition of one drop of ammonium thiocyanate solution. Filter through a weighed filtering crucible (sintered glass) and wash the precipitate 10 to 15 times with a cold solution of ammonium thiocyanate and 5-6 drops of sulphurous acid solution. Finally, wash the precipitate with 20ml alcohol to remove the excess ammonium thiocyanate. Dry the precipitate to constant weight at 110-120 °C. Weigh as CuSCN.

Method of calculation.

$$CuSO_4.5H_2O + 2NH_4SCN \longrightarrow \underset{121.5}{CuSCN} + (NH_4)_2SO_4 + 5H_2O$$

Suppose the weight of CuSCN precipitate is *W* g

121.5 g of CuSCN contains 63.5g Cu

W g ,, ,, ,, $= \frac{63.5 \times W}{121.5}$ g

W g is the weight of copper thiocyanate obtained from 20ml of solution. Hence the amount of Cu^{++} per litre of given solution

$$= \frac{63 \times 50 \times W}{121.5}$$

Exercise. 3.7. *Estimate the amount of ferric ions (Fe^{3+}) in grams per litre of the given Mohr's salt solution.*

Principle. Iron is the second most abundant metallic element. The principle ores are haematite, Fe_2O_3 and magnetite, Fe_3O_4. A large number of elements are found to be present in ores such as manganese, titanium, aluminium, calcium, magnesium, sulphur and carbon in combination. Iron in small amount is very widely distributed in nature, therefore, the analysis for iron in ores, minerals, and manufactured materials, is very frequently required.

Ferrous hydroxide is sufficently soluble and can not be precipitated completely where as ferric hydroxide is highly insoluble and can be precipitated quantitatively. For gravimetric separation iron is therefore, always brought to ferric (+3) state by oxidation of ferrous (+2) with nitric acid, bromine water or hydrogen peroxide. Due to its very small solubility the relative supersaturation of ferric hydroxide during its precipitation is very high. Because of its extensively large surface area the ferric oxide precipitate is likely to get contaminated. For more accurate determination of iron the precipitate of ferric hydroxide formed is dissolved in hydrochloric acid and then reprecipitated from this solution. Contamination can further be reduced if precipitation is done at a temperature near to its boiling point.

$$Fe^{++} \xrightarrow{HNO_3} Fe^{+++} + e^-$$

$$Fe^{+++} + 3NH_4OH \longrightarrow \underset{ppt}{Fe(OH)_3} + 3NH_4^+$$

The precipitate is finally dried and weighed.

Procedure. Pipette out 20ml of the Mohr salt solution into a 400ml corning beaker add 1ml of conc. HCl and 3-4ml of conc. HNO_3. Boil the solution for few minutes until it acquires a deep yellow colour. Test for the complete oxidation of ferrous to ferric state with the glass rod dipping it in a solution of potassium ferricyanide solution, if no blue colour is obtained, the oxdation is complete. Dilute to

150-200ml with distilled water and heat to boiling. To the hot solution add a solution of ammonia (1:1) dropwise with constant stirring till the solution smells strongly of ammonia. Now add 2ml of ammonical paper pulp. Stir with a glass rod. Filter the solution hot using Whatman No. 41 filter paper. Wash the precipitate on the filter paper with 1 per cent hot solution of ammonium nitrate 4-5 times. Test for the complete removal of sulphate ions in the washing by adding 4-5 drops of barium chloride solutions. Dry the precipitate on a metallic cone. Now fold the filter paper with the precipitate and transfer it to a weighed crucible. First heat with a low flame and when paper is charred increase the flame using Meker burner for half an hour. Cool the crucible first in air and then in a desiccator. Weigh the crucible along with the precipitate accurately. Repeat the process of heating for 10-15 minutes till the weight is constant. Record the observations. Let W be the weight of ferric oxide precipitate.

Preparation of paper pulp. Cut a gravimetric filter paper into small pieces add 3-4ml of dil. HNO_3 in a conical flask. Heat the contents gently till it is converted into pulp. Wash it with water and then add ammonia till it gives smell of ammonia.

Method of calculation. $2FeSO_4(NH)_3\ SO_4.6H_2O = 2Fe = Fe_2O_3$

$$2 \times 392 = 112 = 160$$

160g of $Fe_2O_3 = 784$g of Mohr salt

$$Wg \text{ of } Fe_2O_3 = \frac{784}{160} \times W$$

Since Wg is the weight of Fe_2O_3 obtained from 20ml of the solution. Hence, the amount of Mohr salt per litre of the given solution

$$= \frac{784 \times W \times 50}{160}\ g.$$

Precautions. 1. Oxidise the ferrous ions to ferric state to ensure complete precipitation.

2. The precipitation should be carried out in the presence of little HCl and in the hot concentrated solution. In the absence of HCl ferric salt is easily hydrolysed.

3. Since ferric hydroxide is gelatinous, it is difficult to filter as it clogs the pores of the filter paper. Paper pulp is added to increase the rate of filteration.

4. Wash the precipitate with 1 per cent ammonium nitrate solution to prevent peptisation.

Result. The amount of Mohr salt per liter of the given solution was found to be. . . .*g/l.*

4

Qualitative Inorganic .Analysis

4.1. INTRODUCTION

Qualitative chemical analysis is the identification of the constituents of a substance, mixture of substances, solùtions, or group of elements, combined with one another. Two broad subdivisions of the field are recognised: (*a*) qualitative inorganic analysis; (*b*) qualitative organic analysis.

In this chapter we shall deal with the elementary qualitative inorganic analysis. It is interesting to note that the first scheme of separation of common metals (as cations) was devised in 1840. This scheme had, as its core, the isolation of groups of cations, through precipitation of certain insoluble salts. A number of modifications of this scheme have been devised. These classical method of qualitative identification are seldom used as such in industrial laboratories, because they are too involved and time consuming. Practical qualitative analysis is now performed mainly by means of spot tests or through the use of modern instruments. In the present scheme of analysis chemical approach is still retained, although it has been modified so as to obtain a sharper separation of groups, through this approach the student will learn the methods of practical value and will benefit from association with systematic study of chemistry of common anions and cations.

4.2. PRINCIPLES OF QUALITATIVE ANALYSIS

Qualitative inorganic analysis generally depends on the isolation of the given species of ion through precipitation from water solution. The use is made of the varying solubilities of common compounds. For example, calcium chloride is highly soluble in water, calcium sulphate is only moderately soluble in water and silver chloride is insoluble.

The degree of solubility serves as the basis for the separation of ions into different groups expressed in terms of its solubility product value.

Nernst, a German Chemist, discovered a mathematical relationship that exists when a solid salt is in contact with a saturated solution of its ions. His observations are stated in the form of solubility product principle as under:

"In a saturated solution of a slightly soluble salt the product of the concentrations of the ions raised to the powers corresponding to their respective concentration-coefficients is a constant, called the solubility product constant."

The solubility product is valid only for a definite temperature, for accurate work activities should be used which refer to the effective concentration of an ion. For ordinary calculations, however, term, concentration, can be employed.

For example, the solubility product of silver chloride can be expressed from the following equilibria:

$$AgCl(s) = Ag^+ + Cl^-$$

since the coefficients of Ag^+ and Cl^- are both one, solubility product $K_{AgCl} = [Ag^+][Cl^-]$

Here $[Ag^+]$ represent the molar concentration of silver in the solution and $[Cl^-]$ is the molar concentration of chloride ions.

Since the coefficients for the Pb^{++} and Cl^- are one and two respectively, $K_{PbCl_2} = [Pb^{++}] \times [Cl^-]^2$

The solubility product principle is very useful in quantitative chemistry, i.e., in the gravimetric estimation of ions and in qualitative analysis, for classifying cations into different groups.

4.3. COMMON ION EFFECT

Consider the equilibrium dissociation of acetic acid which proceeds according to the following equation:

$$HAc \rightleftharpoons H^+ + Ac^-$$

The hydrogen and acetate ions are the dissociation products. If some acetate ions are now added, this would shift the equilibrium to the left, i.e. some of the hydrogen ions will combine with the acetate ions to form molecules of acetic acid. The effective acidity of the solution will depend on its dissociation as under:

$$\frac{[H^+][Ac^-]}{[HAc]} = K$$

We know that the ratio of reactants and products must always be equal to the same number, $K_{\text{Acetic acid}}$. Therefore, if the $[H^+]$ is increased, $[Ac^-]$ must decrease and $[HAc]$ increases, so as to maintain $K_{\text{Acetic acid}}$ constant. This effect is known as common ion effect and is made use of in qualitative analysis.

4.4. HYDROGEN ION CONCENTRATION (pH)

Hydrogen ion concentration plays a very important role in chemistry. A slight variation in its concentration is very critical sometimes. Therefore, special method is used for expressing the hydrogen ion concentration.

Water, which itself is involved in reaction is exceedingly weak electrolyte and dissociates as follows:

$$H_2O = H^+ + OH^-$$

Applying the law of Mass action,

$$\frac{[H^+][OH^-]}{[H_2O]} = K$$

since the concentration of undissociated water is constant at a given temperature,

or
$$\frac{[H^+][OH^-]}{k} = K$$

$$[H^+][OH^-] = k.K = K_w$$

The value of K_w has been found to be 1×10^{-14} at 25°C, and for neutral system like water

$$[H^+] = [OH^-] = 1 \times 10^{-7} \text{ mole per litre.}$$

The hydrogen ion concentration of neutral water is therefore, equal to, 1×10^{-7} mole per litre.

Sörensen suggested that the H^+ concentration should be designated as the power of 10, except that the powers or exponents should be given as positive numbers. It is defined as;

$$pH = -\log[H^+]$$

He has given a scale for measuring the hydrogen ion concentration, known as pH scale. On this scale the pH of one molar acid is 0 and that of one molar base it is 14. A neutral solution, therefore, has a pH of 7.

A solution which is resistant to the changes in hydrogen ion concentration is known as Buffer solution. This is sometimes necessary for fixing the level of acidity in a solution.

4.5. DRY TEST ANALYSIS

These tests are very useful for the qualitative analysis. The tests are carried out with the dry mixture. Although these dry tests do not give any conclusive evidence, yet afford certain valuable information which are of immense help in the correct identification of the radicals.

Physical observations. Examination of smell, density, and colour of the mixture sometimes gives valuable clues regarding the nature of some acid and basic radicals.

TABLE 4.1.
Results of Physical Observations

Observations	*Inference*
1. White mixture	Cr, Mn, Fe, Co, Mn and Cu are absent.
2. If mixture is coloured	
(*i*) Dark green	Chromium
(*ii*) Light Pink	Manganese
(*iii*) Light green	Ferrous
(*iv*) Yellow or brown	Ferric
(*v*) Deep red or pink	Cobalt
(*vi*) Blue or green	Copper or nickel salt
3. Smell: Rub a pinch of mixture between fingers and smell	
(*i*) Smell of vinegar	Acetate
(*ii*) Smell of H_2S	Sulphide
(*iii*) Smell of Ammonia	Ammonium salt

Dry heating test. Take 0.5g mixture in a dry test tube and heat. Note down the following observations:

(*i*) Evolution of a gas, (*ii*) Colour change and nature of residue, (*iii*) Fusion or melting, (*iv*) Sublimate formation, (*v*) Swelling or intumescence, (*vi*) cracking sound. The results of dry heating tests are given in Table 4.2.

TABLE 4.2
Dry Heating Test

Observations	*Inference*	*Chemical Reaction*
CO_2: Colourless turns lime water milky	Carbonate, bicarbonate oxalate and tartarate	$CaCO_3 \rightarrow CaO + CO_2$ $Ca(HCO_3)_2 \rightarrow CaO + H_2O + CO_2$ $(COO)_2Ca \rightarrow CaO + CO_2 + CO$
H_2S: Rotten eggs smell, turns lead acetate black	Sulphide	$Na_2S + Pb(CH_3COO)_2 \rightarrow PbS + 2\,CH_3COONa$ (Black)
SO_2: Pungent odour	Sulphite or thiosulphate	$CaSO_3 \rightarrow CaO + SO_2$
CH_3COOH: Vinegar smell (ripe fruit)	An acetate	$CH_3COONa + H_2O \rightarrow CH_3COOH + NaOH$
HCl or Cl_2: Pungent smell gives white fumes with ammonia	Chlorides	$ZnCl_2 .\ 6H_2O \rightarrow Zn\ (OH)Cl + 5H_2O + HCl$
NO_2: Brown vapour turns $FeSO_4$ solution black	Nitrites or Nitrates	$Ca(NO_3)_2 \rightarrow CaO + NO_2 + O_2$
Br_2: Reddish brown turns starch paper yellow	Bromide	$2KBr + H_2O \rightarrow 2KOH + Br_2$
I_2: Violet (turns starch paper blue)	Iodides	$2NaI + H_2O \rightarrow 2NaOH + I_2$
NH_3: Characteristic gives sense white fumes with Conc. HCl.	Ammonium salt	$(NH_4)_2SO_4 \rightarrow NH_4HSO_4 + NH_3$

Change in colour. Certain substances change their colour on heating but regain their original colour on cooling. Some examples are given in table 4.3.

TABLE 4.3
Characteristic colour changes in Hot and Cold

Cold	*Hot*	*Inference*
Buff	Brown red	PbO
Red	Chocolate	Pb_3O_4
Red	Black	HgO
Scarlet	Black	HgS
Crimson	Yellow	HgI_2
Yellow	Brown	Bi_2O_3
White	Yellowish brown	SnO_2
White	Orange yellow	ZnO

Violet	Green	Chromic salts
Yellow	Brownish black	$FeCl_3.6H_2O$
Red	Violet	$CoI_2.6H_2O$
Red	Green	$CoBr_2.6H_2O$
Blue	White	$CuSO_4.5H_2O$

Flame Test

Principle. On heating some volatile metal chlorides in an oxidising flame break into ions. The cation at this stage imparts characteristic colour to the flame.

Procedure. A platinum wire is used for this purpose. Clean this wire by repeatedly dipping in conc. HCl and subsequently heating in an nonluminous flame (oxidising) until it imparts no colour to the flame. Make a paste of the mixture in conc. HCl dip this wire in the paste and heat in an oxidising flame.

Table 4.4 lists the characteristic colours of some metal ions in the Bunsen flame.

TABLE 4.4

Flame Test Observations

Colour	*Blue Glass*	*Inference*
Golden yellow	No colour	Sodium
Pink violet	Pink	Potassium
Dark green	Bluish green	Copper
Brick red	light green	Calcium
Deep red	Purple	Strontium
Grassy	Bluish green	Barium

Borax Bead Test

Principle. Borax ($Na_2B_4O_7.10H_2O$) on heating loses its water of crystallization and swells up into a white porous mass. On further heating it is converted into a clear transparent glassy bead containing sodium metaborate and boric anhydride.

$$\underset{\text{(Borax)}}{Na_2B_4O_7.10H_2O} \rightarrow \underset{\substack{\text{sodium}\\\text{metaborate}}}{2NaBO_2} + \underset{\substack{\text{boric-}\\\text{anhydride}}}{B_2O_3} + 10H_2O$$

The bead is moistened with a drop of water, then dipped into the finely powdered substance and heated in an oxidising flame. Boric anhydride, being non-volatile, displaces more volatile acidic oxides, combines with basic oxides present, to form coloured metaborates. Thus with chromium, manganese, iron, cobalt, nickel and copper salts, the following reactions occur in oxidising flame.

$$CoSO_4 + B_2O_3 \longrightarrow \underset{\substack{\text{Cobalt metaborate}\\ \text{(blue bead)}}}{Co(BO_2)_2} + SO_3$$

$$NiSO_4 + B_2O_3 \longrightarrow \underset{\substack{\text{Nickel metaborate}\\ \text{(brown bead)}}}{Ni(BO_2)_2} + SO_3$$

$$CuSO_4 + B_2O_3 \longrightarrow \underset{\substack{\text{Cupric metaborate}\\ \text{(blue bead)}}}{Cu(BO_2)_2} + SO_3$$

In the reducing flame (i.e., in the presence of carbon), the reduction of higher metaborates takes place into metallic state. For example:

$$2Cu(BO_2)_2 + C \longrightarrow \underset{\text{Cuprous metaborate}}{2CuBO_2} + B_2O_3 + CO$$

$$2CuBO_2 + C \longrightarrow \underset{\text{Brown}}{2Cu} + B_2O_3 + CO$$

Procedure. Take a platinum wire and coil it into a small loop. Heat it in the Bunsen flame until it is red hot and then quickly dip into powdered borax, $Na_2B_4O_7.10H_2O$. Heat it again strongly, in the outer oxidising flame till a clear transparent bead is obtained. The bead is moistened and dipped into the finely powdered substance till it adheres to the bead. The bead and adhering substance is heated, first in the lower reducing flame allowed to cool and, note down the colour. It is then heated in the lower oxidising flame allowed to cool and observe the colour. Note the colour of bead in each case.

Table 4.5 gives the characteristic colours of some metal beads.

TABLE 4.5

Characteristic Colours of Borax Beads

Reducing flame	*Colour of the Bead in Oxidising flame*	*Inference*
Bright green	Bright green	Chromium
Colourless	Light pink	Manganese
Green	Yellow	Iron
Blue	Deep blue	Cobalt
Grey	Brown	Nickel
Brown	Bluish green	Copper

Note. (*i*) This test is applicable only for coloured salts. (*ii*) It is important to employ a minute amount of substance as otherwise the bead will become dark and opaque.

Charcoal Cavity Test

Principle. On heating a pinch of the mixture, with fusion mixture

($Na_2CO_3 + KNO_3$) in a charcoal cavity, the metal is converted into carbonate and finally decomposes into their respective oxides.

$$Pb(NO_3)_2 + Na_2CO_3 \longrightarrow PbCO_3 + 2NaNO_3$$
$$PbCO_3 \longrightarrow PbO + CO_2$$

These oxides are reduced into metal in the presence of carbon.

$$PbO + C \longrightarrow Pb + CO$$

It has been observed that oxides of more electropositive metals MgO, ZnO and CaO are not reduced by carbon. The metal oxides reduce into its metallic form by heating with cobalt nitrate solution in the reducing flame. The reaction may be written as follows:

$$2Co(NO_3)_2 \longrightarrow 2CoO + O_2 + 4NO_2$$
$$ZnO + CoO \longrightarrow CoZnO_2 \text{ (green)}$$
$$MgO + CoO \longrightarrow CoO.MgO \text{ (pink)}$$

Procedure. Take a pinch of mixture in a charcoal cavity which is prepared with the help of knife in the charcoal block and moisten the mixture with a drop of water. Heat it in the reducing flame with the help of blow pipe for 2-3 minutes and note down the colour, compare the colour with the Table 4.6 given below:

TABLE 4.6
Charcoal Cavity Test

Observation	*Inference*
Grey residue	Mn, Fe, Co, Ni salts
White infusible	Mn, Fe, Ni, Cu, Zn, Bi, Ag may be absent.
Brown	Cd
Red	Cu
	Cobalt-Nitrate Test
Dirty Pink	Mg salts
Black	CoO
Blue	Al
Green	Zn

4.6 ANION ANALYSIS

The systematic qualitative analysis of inorganic mixture consists in analysing for its anionic and cationic contents. It is always advisable to analyse the mixture first for the anions and then for the cations. However, the systematic analysis of the anions is much more difficult than that of the cations, mainly due to the greater reactivity of the anions. For anion analysis, the mixture is dissolved in water, if soluble, the solution is employed as such, otherwise the anions are brought into solution by preparing sodium carbonate extract.

Preparation of water extract. Take 1 or 2 g of mixture in a boiling tube and 10-20ml of distilled water and boil it for 5 minutes. Filter and label the filtrate as water extract. All nitrites, nitrates, thiosulphates and acetates can be tested by the water extract since they are water soluble.

Preparation of sodium carbonate extract. Take 0.5-1g of the given mixture in a beaker. Add 1.5-3gm (four to five times the amount of mixture taken) of Na_2CO_3 and about 10-15ml of distilled water to the beaker. Heat to boiling till the volume is reduced to nearly two third. Allow to cool and filter. The filtrate, thus obtained, is known as sodium carbonate extract and should be used for the analysis of anions. The scheme for the systematic analysis of anions, has been divided, into six groups as shown in Table 4.7.

TABLE 4.7
Anion Groups

Sl. No.	*Group*	*Group Reagent and Color*	*Anions*
I	Diphenylamine group	Diphenylamine in conc. H_2SO_4, blue colour;	NO_2^-, NO_3^-, CrO_4^{2-}
II	Barium Chloride group	Barium Chloride solution; white ppt.	SO_3^{2-} and SO_4^{2-}
III	Sodium Nitroprusside group	Sodium nitroprusside purple colour	S^{2-}, SO_3^{2-}, $S_2O_3^{2}$ and SO_4^{2-}
IV	Silver nitrate	Silver nitrate solution white or yellow ppt.	Cl^-, Br^- and I^-
V	Calcium Chloride group	Calcium Chloride white ppt.	F^- and $C_2O_4^{2-}$
VI	Individual Test	No reagent	CO_3^{2-}, CH_3COO^- PO_4^{3-} and BO_3^{3-}

Group I : Diphenylamine Group. Nitrate (NO_3^-). Take 2 drops of Na_2CO_3 extract in a test tube. Acidify this with dil. H_2SO_4. Add 2-3 drops of diphenylamine (in conc. H_2SO_4) reagent, formation of blue colour confirms nitrate.

(*a*) *Brown ring test*. Take 0.5ml of Na_2CO_3 extract. Acidify this with dil. H_2SO_4, and add about 1ml of freshly prepared $FeSO_4$ solution followed by the addition of 1ml of conc. H_2SO_4 from the side of the test tube. Formation of brown ring at the junction of the two liquids confirms nitrate. The chemical reaction which occurs can be mbolised as:

$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$$

$$FeSO_4 + NO \rightarrow \underset{\text{(Brown ring product)}}{FeSO_4NO}$$

(*b*) *Spot test*. Take 2 drops of water extract of the mixture in a test tube. Add 2 drops of sulphanilic acid in acetic acid followed by the addition of 2 drops of α-naphthylamine. Add a small amount of zinc dust. Formation of red colour confirms nitrate.

Group II : Barium Chloride Group. Sulphate (SO_4^{2-}). Acidify 0.5ml Na_2CO_3 extract with dil. HCl. Add 0.5-1.0ml of $BaCl_2$ solution. Formation of a white precipitate insoluble in conc. HCl or conc. HNO_3 confirms sulphate.

$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2NaCl$$

Group III : Nitroprusside Group. Sulphide, sulphite and sulphate (S^{2-}, SO_3^{2-}, SO_4^{2-}).

Sulphide (S^{2-}). (*a*) Take 2-3 drops of sodium carbonate extract and acidify with dil. acetic acid. Add 2-3 drops of lead acetate solution. Formation of black precipitate of PbS confirms sulphide.

$$Pb(CH_3COO)_2 + Na_2S \longrightarrow \underset{\text{(Black)}}{PbS} + 2CH_3COONa$$

(*b*) Take 0.5ml of Na_2CO_3 extract in a test tube. Add about 1ml dil. HCl and immediately cover the mouth of the test tube with a moistened lead acetate paper. Formation of brown to black stain on the filter paper confirms sulphide.

Sulphite (SO_3^{2-}). (*a*) *Dry Test*: To a small amount of the mixture in a text tube, add few drops of dil. H_2SO_4. Note the smell of the gas. If the gas is colourless with pungent smell, it may be sulphite.

(*b*) Take 0.5ml of Na_2CO_3 extract in a test tube, acidify by adding dil. HCl. Add 0.5-1.0ml of barium chloride solution. Appearance of a white precipitate may be due to the presence of sulphate. Filter and to the filtrate add about 1ml of chlorine of bromine water. Keep the test tube aside for some time. Formation of white precipitate confirms sulphite.

$$SO_3^{2-} + Cl_2 + H_2O \longrightarrow SO_4^{2-} + 2HCl$$

$$SO_4^{2-} + BaCl_2 \longrightarrow \underset{\text{(White ppt.)}}{BaSO_4} + 2Cl^-$$

(*c*) To a small amount of the mixture in a test tube add 2 drops of $K_2Cr_2O_7$ solution Add 0.5ml-1.0ml dil H_2SO_4 and note the change in colour of the solution. Yellow colour of dichromate changing to green, confirms sulphite.

$$3K_2SO_3+K_2Cr_2O_7+4H_2SO_4 \longrightarrow \underset{\text{(Green)}}{Cr_2(SO_4)_3}+4K_2SO_4+4H_2O$$

Group IV: Silver Nitrate Group. Chloride, Bromide and Iodide (Cl^-, Br^-, I^-)

Chloride (Cl^-). (*a*) Take 1.0ml of sodium carbonate extract in a test tube, acidify with dil. HNO_3. Add 4-5 drops of silver nitrate solution. Formation of white precipitate which dissolves in excess of ammonium hydroxide solution confirms chloride.

$$AgNO_3+NaCl \longrightarrow \underset{\text{(White)}}{AgCl\downarrow}+NaNO_3$$

$$AgCl+2NH_4OH \longrightarrow \underset{\substack{\text{(Soluble}\\ \text{Complex)}}}{Ag(NH_3)_2Cl}+2H_2O.$$

(*b*) *Chromyl chloride test*. To about 0.1g of the solid mixture in a dry test tube, add about 0.3g of solid $K_2Cr_2O_7$ and about 2ml of conc. H_2SO_4. Heat the contents of the tube and pass the evolved gas in another test-tube containing about 2ml of NaOH solution. Acidify this alkaline solution with dil. acetic acid. Add about 1ml of lead acetate solution. Formation of yellow precipitate of $PbCrO_4$ confirms chloride. The reactions can be symbolised as:

$$K_2Cr_2O_7+4NaCl+H_2SO_4 \longrightarrow 2CrO_2Cl_2+2KHSO_4+4NaHSO_4+3H_2O$$

$$CrO_2Cl_2+4NaOH \longrightarrow Na_2CrO_4+2NaCl+2H_2O$$

$$Na_2CrO_4+Pb(CH_3COO)_2 \longrightarrow \underset{\text{(Yellow)}}{PbCrO_4}+2CH_3COONa$$

Note. This test should be performed only when bromide is absent, covalent compounds do not give this test, e.g., Hg_2Cl_2.

Bromide (Br^-). (*a*) Acidify 4-5 drops of Na_2CO_3 extract with dil. HNO_3, add 4-5 drops of silver nitrate solution. Formation of pale yellow precipitate which is partially soluble in ammonium hydroxide, shows the presence of bromide.

(*b*) Acidify 4-5 drops of Na_2CO_3 extract with dil. HNO_3. Add about 1ml of CS_2, CCl_4, $CHCl_3$ or C_6H_6 followed by the addition of 2ml of conc. HNO_3 or 1ml of $KMnO_4$ solution. Shake the solution and allow the two layers to separate, the organic layer acquires the orange colour. This confirms bromide. The following chemical reaction takes place:

$$2NaBr+4HNO_3 \longrightarrow 2NaNO_3+Br_2+2H_2O+2NO_2$$

Iodide (I^-). (*a*) Take 4-5 drops of sodium carbonate extract in a test tube, acidify with dil. HNO_3. Add 4-5 drops of silver nitrate solution. Formation of yellow precipitate of AgI insoluble in ammonium hydroxide indicates the presence of iodide.

(*b*) Take 10ml of Na_2CO_3 extract in a test tube and acidify with dil. HNO_3 or dil. H_2SO_4. Add 1-2ml of CCl_4, $CHCl_3$, CS_2 or C_6H_6 followed by the addition of 1ml of solution or chlorine water and allow the two layers to separate. If the organic layer acquires the violet colour, it confirms the presence of iodide.

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

$$I_2 + CCl_4 \longrightarrow \text{Soluble (Violet colour)}$$

(*c*) Take 0.5ml of Na_2CO_3 extract in a test-tube and acidify with dil. H_2SO_4. Add about 0.5gm of solid sodium nitrite and heat. Formation of violet vapours due to iodine confirms iodide.

$$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$$

$$NaI + H_2SO_4 \longrightarrow NaHSO_4 + HI$$

$$2HNO_2 + 2HI \longrightarrow I_2 + 2NO + 2H_2O$$

Group V: Calcium Chloride Group. Oxalate and fluoride ($C_2O_4^{2-}$, F^-)

Take about 2ml of Sodium Carbonate extract and acidify it with dil. acetic acid. Add 1-2 ml of calcium chloride solution, formation of a white precipitate indicates the presence of fluoride and oxalate.

Treat a portion of the precipitate with dil. H_2SO_4, the oxalate will dissolve and fluoride remains insoluble. Centrifuge or filter. To a portion of the centrifugate add dil. $KMnO_4$ dropwise which gets decolorised confirms oxalate, $C_2O_4^{2-}$. Residue if any indicates the presence of fluoride in the given mixture.

Individual Tests

Phosphate (PO_4^{3-}). Take 0.5ml of sodium carbonate extract in a test tube, acidify with dil. HNO_3. Add 1ml of ammonium molybdate solution followed by the addition of 1ml of conc. HNO_3. Yellow precipitate formed on heating confirms phosphate.

$$Na_3PO_4 + 24HNO_3 + 12(NH_4)_2MoO_4 \longrightarrow 3NaNO_3 + 21NH_4NO_3 + 12H_2O + \underset{\text{(Yellow colour)}}{(NH_4)_3PO_4.12MoO_3}$$

The same test can also be performed with original mixture. If As^{+++} is present in the mixture then test for phosphate should be performed after removal of As^{+++}.

Oxalate, $C_2O_4^{2-}$. Acidify 0.5 ml of sodium carbonate extract with dil. acetic acid, boil to expel Carbondioxide, add 0.5 ml of Calcium Chloride solution, warm. Filter or centrifuge, divide the residue into two portions.

(*i*) To one portion of the above add one drop of $KMnO_4$ solution, 1 ml of dil. H_2SO_4 and warm. Disappearance of pink colour confirms oxalate.

(*ii*) To the remaining portion of the residue add a tiny crystal of diphenylamine and 2 ml of syrupy phosphoric acid. Heat the test tube carefully over a free flame. Appearance of blue colour, confirms oxalate.

Carbonate (CO_3^{2-}). To about 0.1gm of the solid mixture, add about 1ml of dil. H_2SO_4. Formation of brisk effervescene confirms carbonate. Pass carbon dioxide gas evolved into another test tube, containing $Ca(OH)_2$ or $Ba(OH)_2$ solution. Formation of white precipitate of calcium carbonate or barium carbonate confirms carbonate.

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$
$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

Acetate (CH_3COO^-). (*a*) Take 1ml of water extract in a dry clean test tube, add freshly prepared neutral $FeCl_3$ solution. Appearence of brick red colour indicates acetate. Add 5ml of water and boil it, a brown coloured precipitate confirms acetate,

$$3CH_3COO^- + Fe^{3+} \longrightarrow \underset{\text{(Red colour)}}{(CH_3COO)_3Fe}$$
$$(CH_3COO)_3Fe + 2H_2O \longrightarrow \underset{\substack{\text{Basic ferric acetate}\\ \text{(Brown)}}}{Fe(OH)_2CH_3COO} + 2CH_3COOH.$$

Borate (BO_3^{3-}). Take a small amount of mixture in a dry test tube. Add 2ml of conc. H_2SO_4 and 5ml ethyl alcohol. Warm the contents of the tube and ignite the vapour issuing at the mouth. A green-edged flame confirms the presence of borate.

$$Na_2B_4O_7.10H_2O + H_2SO_4 \longrightarrow Na_2SO_4 + 4H_3BO_3$$
$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\substack{\text{(ethyl borate)}\\ \text{(Green)}}}{B(OC_2H_5)_3} + 3H_2O$$

Fluoride (F^-). Take a small amount of mixture in a dry test tube, add to it equal amount of sand and 2ml of conc. H_2SO_4. Heat and hold a moistened glass rod in the vapours. A waxy white gelatinous deposit confirms fluoride,

$$4F^- + 4H^+ + SiO_2 \longrightarrow \underset{\substack{\text{White}\\ \text{fumes}}}{SiF_4} + 2H_2O$$
$$3SiF_4 + 4H_2O \longrightarrow \underset{\substack{\text{Silicic}\\ \text{acid}}}{H_4SiO_4} + \underset{\substack{\text{Hydrofluosilicic acid}\\ \text{waxy deposit}}}{2H_2SiF_6}$$

Tests for the Acid Radicals one in Presence of Other

(*i*) *Cabonate in the presence of sulphite*. Carbonate and sulphite on treatment with dil. H_2SO_4 produce CO_2 and SO_2 respectively. Both SO_2 and CO_2 turn lime water milky

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$
$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 + H_2O$$

Hence, we can not infer that this turbidity is due to either the formation of $CaCO_3$ or $CaSO_3$. In order to test for carbonate the SO_2 liberated is entrapped by adding $K_2Cr_2O_7$ and the residual gas is then passed through lime water for testing CO_2.

$$Cr_2O_7^{2-} + 2H^+ + 3SO_2 \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$$
$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + \underset{\text{(Green)}}{Cr_2(SO_4)_3} + H_2O$$

Take about 0.2g of mixture in a test tube. Add to it equal amount of $K_2Cr_2O_7$ and 2ml of dil. H_2SO_4. Heat the test tube and pass the evolved gas through lime water. If the colour of the lime water turns milky carbonate is confirmed. On the other hand, turning of the solution green, confirms sulphite.

(*ii*) *Sulphide, sulphate, thiosulphate and sulphite.* Take the sodium carbonate extract in a test-tube. Acidify it with dil. acetic acid and add sodium nitroprusside solution. A purple colour indicates the presence of sulphide; when present, take another portion of sodium carbonate extract (10ml) and add excess of solid copper carbonate or cadmium carbonate. The following reactions take place,

$$Na_2S + CuCO_3 \longrightarrow CuS + Na_2CO_3$$
$$Na_2S + CdCO_3 \longrightarrow CdS + Na_2CO_3$$

Filter and acidify the filtrate with dilute HNO_3 and add slight excess of ammonia. Boil off excess of ammonia. Now add an excess of a conc. barium chloride ($BaCl_2$) solution. A white precipitate indicates the presence of sulphite or sulphate according to the following equations:

$$SO_3^{2-} + Ba^{2+} \longrightarrow \underset{\text{(Insoluble)}}{BaSO_3}$$
$$SO_4^{2-} + Ba^{2+} \longrightarrow \underset{\text{(Insoluble)}}{BaSO_4}$$

Filter, the precipitate. Test for the sulphate and sulphite with the precipitate and thiosulphate with the filtrate. Add cold dil. HCl to the precipate, the residue remaining on the filter paper confirms sulphate (SO_4^{2-}).

Take the filtrate in a test tube and add few drops of conc. HNO_3 or bromine water and warm, appearance of a white ppt. confirms sulphite.

$$BaSO_3 + (O) \longrightarrow BaSO_4 \text{ (White ppt)}$$

Test for thiosulphate. To the filtrate add few drops of silver nitrate ($AgNO_3$) solution. A white precipitate, turning yellow, orange, brown and finally black confirms thiosulphate according to the following reactions:

$$S_2O_3^{2-} + 2Ag^+ \longrightarrow Ag_2S_2O_3 \xrightarrow{H_2O} Ag_2S + 2H^+ + SO_4^{2-}$$

(*iii*) *Sulphate in the presence of fluoride*. Fluoride interferes in the test for sulphate with $BaCl_2$, because fluoride reacts with $BaCl_2$ and forms a white precipitate of BaF_2 (insoluble in HCl) even if sulphate is absent. The method given below should be adopted.

Take sodium carbonate extract in a test tube. Acidify it by the addition of dil. CH_3COOH. Carbon dioxide gas evolved is removed by boiling and then add $Pb(CH_3COO)_2$ solution. Appearance of a white precipitate confirms sulphate, according to the following chemical reaction:

$$SO_4^{2-} + Pb^{2+} \longrightarrow \underset{\text{(White ppt)}}{PbSO_4}$$

(*iv*) *Oxalate in presence of carbonate*. On treating the mixture containing carbonate and oxalate with conc. H_2SO_4 carbon dioxide gas is evolved. Hence, we are not able to conclude whether the evolved CO_2 is from oxalate or carbonate. Then following method should be performed.

Treat about 0.5g of mixture in a test tube with dil. H_2SO_4 if there is effervescence, and CO_2 is evolved (which can be tested with lime water) CO_3^{2-} is present. Warm it till there is no more effervescence. Now add a pinch of manganese dioxide and warm. If there is effervescence due to CO_2 gas it confirms oxalate. The chemical reactions are:

$$Na_2C_2O_4 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO + CO_2$$
$$Na_2CO_3 + 2H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2$$
$$Na_2C_2O_4 + MnO_2 + 2H_2SO_4 \rightarrow Na_2SO_4 + MnSO_4 + 2H_2O + 2CO_2$$

(*v*) *Nitrate in presence of nitrite*. Water extract can be used for the confirmation of these anions, since all nitrates and nitrites are soluble in water. Nitrite always interferes with all the tests for nitrate. Consquently in the presence of a nitrite test for nitrate can be made only after destroying the nitrite.

The nitrite is tested as follows:

(*a*) To 2ml of the water extract add 2ml of freshly prepared ferrous sulphate solution and acidify with dil. H_2SO_4. A brown coloured solution confirms nitrite.

$$NaNO_2 + H_2SO_4 \rightarrow NaHSO_4 + HNO_2$$
$$FeSO_4 + 2HNO_2 \rightarrow FeSO_4.NO + H_2O + NO_2$$

(*b*) Acidify a small portion of water extract with dil. HCl or dil. H_2SO_4

and then add a pinch of KI and 2-3 drops of starch. A deep blue coloration confirms nitrite.

$$2KNO_2 + 4HCl + 2KI \rightarrow 4HCl + 2NO + 2H_2O + I_2$$

$$\text{Strach} + I_2 \rightarrow \underset{\text{(Blue)}}{\text{Starch iodide complex}}$$

After the nitrite has been tested, it is decomposed by using urea or NH_4Cl. For this take the water extract of mix. and add 2g of urea or NH_4Cl and 2ml of H_2SO_4 (dil.)

$$NaNO_2 + H_2SO_4 \rightarrow HNO_2 + NaHSO_4$$

$$NH_2CONH_2 + 2HNO_2 \rightarrow CO_2 + 2N_2 + 3H_2O$$

Take a portion of above solution in a test tube and add KI and strach. If no blue colour, the complete removal of nitrite is indicated.

Nitrate can now be tested by following methods:

(*a*) To one part of test solution add 1ml freshly prepared solution of $FeSO_4$ and conc. H_2SO_4 along the side of test tube. A brown ring at the junction of the two liquid layers indicates nitrate.

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

$$2HNO_3 + 3H_2SO_4 + 6FeSO_4 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

$$FeSO_4 + NO \rightarrow FeSO_4NO$$

(*b*) To the other part of the test solution add a small crystal of KI and two drops of starch solution and a pinch of Zn dust. Appearance of blue colour confirms nitrate.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + 2H$$

$$NaNO_3 + H_2SO_4 + 2H \rightarrow NaHSO_4 + HNO_2 + H_2O$$

$$2KI + 2H_2SO_4 + 2HNO_2 \rightarrow 2KHSO_4 + 2NO + 2H_2O + I_2$$

$$I_2 + \text{starch} \longrightarrow \underset{\text{(Blue complex)}}{\text{starch iodide}}$$

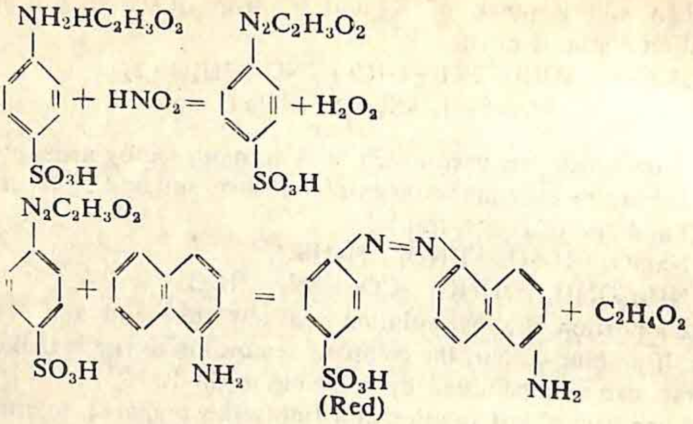
(*vi*) *Nitrate in the presence of bromide and iodide.* It may be noted when nitrate is present along with bromide and iodide then detection of nitrate is difficult.

During the dry test, when mixture is treated with hot conc. H_2SO_4, it is not possible to distinguish between the vapours of NO_2, Br_2 and I_2. Further the ring test is also not applicable. Hence, the detection of nitrate in the presence of bromide or iodide is done by following test:

Take two drops of water extract in a groove tile and add to it one drop of sulphanilic acid and one drop of α-naphthylamine, add one drop of H_2SO_4 and a pinch of zinc dust. Formation of red rose colour confirms nitrate.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + 2H$$

$$NaNO_3 + H_2SO_4 + 2H \rightarrow NaHSO_4 + HNO_2 + H_2O$$



4.7. CATION ANALYSIS

An ideal scheme of qualitative analysis would provide distinct test that would help to identify a given ion when found alone or in presence of a large number of other ions. The anions can be analysed by preparing their sodium carbonate extract. However, there is not ideal method for the analysis of cations. The ions are classified into small groups on the basis of given property which is common to small number of them. The ions in a given group may be separated into subgroups and the presence of the ion may be established on the basis of the solubility of its ion, or colour of a solution, or precipitate. The cations are brought into the solution from an unknown mixture, salt or an alloy by treating with any one of the following solvents in hot and cold, which must be tried in the following order of preference:

(*i*) Water

(*ii*) Hydrochloric acid (dil.)

(*iii*) Hydrochloric acid (conc.)

(*iv*) Nitric acid (dil.)

(*v*) Nitric acid (conc.)

Note. Try to avoid the use of HNO_3 for making the solution of the mixture, as it interferes in the analysis of certain cations.

The analysis of cations has been divided into several different groups on the basis of solubility product of the insoluble compounds formed by them, on treating with different reagents. The two cations K^+ and NH_4^+ should be tested before starting the general scheme of cation analysis. This step is done, since the salts of K^+ and NH_4^+ are generally used in the general scheme. The undermentioned table gives the general scheme of analysis from Group I to Group VI.

Group No.	*Group reagent*	*Group members and nature of the precipitate*
Zero	—	K^+, NH_4^+
1.	Dil. HCl	$PbCl_2$, AgCl, Hg_2Cl_2
2.	H_2S in HCl medium	HgS, PbS, Bi_2S_3, CuS, CdS, As_2S, Sb_2S_3, SnS_2
3.	NH_4OH in presence of NH_4Cl	$Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$
4.	H_2S in ammonical medium	ZnS, MnS, NiS, CoS
5.	$(NH_4)_2CO_3$ in ammonical	$BaCO_3$, $SrCO_3$, $CaCO_3$
6.	Na_2HPO_4	$Mg_3(PO_4)_2$

Preparation of original solution (O.S.) for cation analysis. The solution of the given sample for analysis, obtained, by dissolving in any of the above mentioned solvents will be called original solution (O.S.). This term has been used in the general cation scheme throughout. For making the O.S. of the given sample, the solubility of the given sample is tested as follows:

(1) Take small amount of the given sample in test tube and add about 1-2ml of deionised or distilled water. Shake the contents of the test tube and note the solubility of the given sample. If it is soluble, a clear solution must be obtained and if the sample remains insoluble, then heat the contents of the test tube to boiling, again check, if a clear solution is obtained or not. If the given sample remains insoluble in water then proceed as follows to make the O.S. in any of the acid.

(2) Take small amount of the given sample in a test tube and add 1-2 ml of conc. HCl. Shake the contents and note the solubility. Incase, a clear solution is not obtained, heat the contents of the given tube and again note the solubility. Formation of a clear solution indicates the solubility of the given sample in conc. HCl. The same precedure may be followed with dil. HCl.

(3) Take small amount of the given sample in a test tube. Add 1-2 ml of conc. HNO_3. Shake the contents of the test tube. Note the solubility. A clear solution indicates the solubility in conc. HNO_3. If some residue is left, check the solubility after heating the test tube containing the given sample and conc. HNO_3. In case the given sample is soluble in conc. HNO_3, a clear solution will be obtained.

The preceding procedure may be repeated with dil. HNO_3. If the given sample is insoluble in conc. HNO_3 in cold and hot conditions.

Note. If the given sample is found to be soluble in both nitric and hydrochloric acid, one should always choose hydrocloric acid to prepare original solution (O.S.)

After having established the solubility of the given sample by performing the above tests, the student should now prepare original solution of the sample by the following procedure:

Take about 0.1gm of the given sample in a test tube and dissolve it in 10ml of the suitable solvent. This will be hence forth known as original solution (O.S.)

Analysis of Cations. Zero group, Ammonium (NH_4^+) and Potassium (K^+)

Ammonium (NH_4^+). (*i*) Take small amount of the given sample in a test tube and add about 2ml of 10 per cent NaOH solution. Heat the contents of the test tube and note the smell of the gas. Ammonical smell indicates the presence of ammonium (NH_4^+)

$$NH_4Cl + NaOH \rightarrow NH_3 + H_2O + NaCl$$

(*ii*) Pass the evolved gas into another test tube containing about 1-2ml of Nessler's reagent. Formation of brown colour confirms ammonium (NH_4^+).

Potassium (K^+). (*i*) Take a small amount of the given sample in a test tube and heat it after adding about 1-2ml of distilled water. Filter if necessary. To the filtrate add 1-2ml of acetic acid and 4-5 drops of freshly prepared sodium cobaltinitrite solution. Formation of a yellow crystalline precipitate shows the presence of potassium (K^+)

$$Na_3[Co(NO_2)_6] + 2KCl \longrightarrow \underset{\text{(Yellow ppt.)}}{K_2Na[Co(NO_2)_6]} + NaCl$$

(*ii*) Filter the above yellow coloured precipitate. Take the residue on a watch glass and mix with about 0.5ml of conc. HCl perform the flame test as follows:

Dip the platinum-wire with the above paste and bring it in the flame, observe the colour of the flame. Violet colour (red through double blue glass (Co glass) confirms potasssium (K^+).

Systematic analysis of Group I cations. $PbCl_2$, $AgCl$, Hg_2Cl_2.

Procedure. To the O.S. prepared above (if given sample is soluble in dil. or conc. hydrochloric acid, the cations of group I are taken to be absent) add dil. HCl till no more ppt. of cations of group I. Filter or centrifuge. Keep the filterate or centrifugate for the analysis of subsequent group radicals. Wash the white precipitate with cold water. Take white precipitate in a test tube. Add about 3-4ml of distilled water and heat to boiling for 2-3 minutes. Filter or centrifuge while the solution is hot. This is shown in flow sheet No. 1. Refer to table 4.8 for the systematic identification of group I cations.

TABLE 4.8

<table>
<tr>
<td>Hot filtrate or centrifugate This may contain $PbCl_2$ devide this into two parts</td>
<td colspan="2">Residue: This may contain AgCl and Hg_2Cl_2. Take this residue in a test tube and treat with 2-3ml of NH_4OH solution. Warm this slightly. Filter or centrifuge.</td>
</tr>
<tr>
<td>To one part of the solution add about 1ml of acetic acid and add 1ml of K_2CrO_4 solution, formation of yellow precipitate confirms lead.
$PbCl_2+K_2CrO_4 \rightarrow PbCrO_4+2KCl$
(Yellow)
To the second part, add about 1ml KI solution
Formation of yellow precipitate of PbI_2
$PbCl_2+2KI \rightarrow PbI_2+2KCl$ confirms lead.</td>
<td>Filterate or centrifugate: may contain AgCl, as $Ag(NH_3)_2Cl$
To the above solution containing silver as complex salt, add a few drops of dil. HNO_3 Formation of white precipitate of AgCl confirms silver.
$AgCl+2NH_4OH \rightarrow Ag(NH_3)_2Cl+2H_2O$
$Ag(NH_3)_2Cl+2HNO_3 \rightarrow AgCl+2NH_4NO_3$
(White ppt)</td>
<td>Residue: May contain Hg_2Cl_2 as $Hg(NH_2)Cl$ (Black)
$Hg_2Cl_2+2NH_4OH \rightarrow 2Hg(NH_2)Cl+Hg+$
(Black ppt)
NH_4Cl+2H_2O
Take residue in a test tube. Add to this 1-2ml aqua regia ($HCl:HNO_3$ 3:1) and heat to dissolve. Dilute this by adding 1-2ml of water and divide into two parts.
$HNO_3+HCl \rightarrow NOCl+2Cl+2H_2O$
$Hg(NH_2)Cl+Hg+2Cl+2HCl \rightarrow 2HgCl_2+NH_4Cl$
To one part, add few drops of $SnCl_2$ solution when white ppt is obtained. Add excess of $SnCl_2$ solution. Heat the solution white precipitate turns black Confirms mercury.
$2HgCl_2+SnCl_2 \rightarrow Hg_2Cl_2+SnCl_4$
(White ppt)
$Hg_2Cl_2+SnCl_2 \rightarrow 2Hg+SnCl_4$
(Black ppt)
To the other portion add</td>
</tr>
</table>

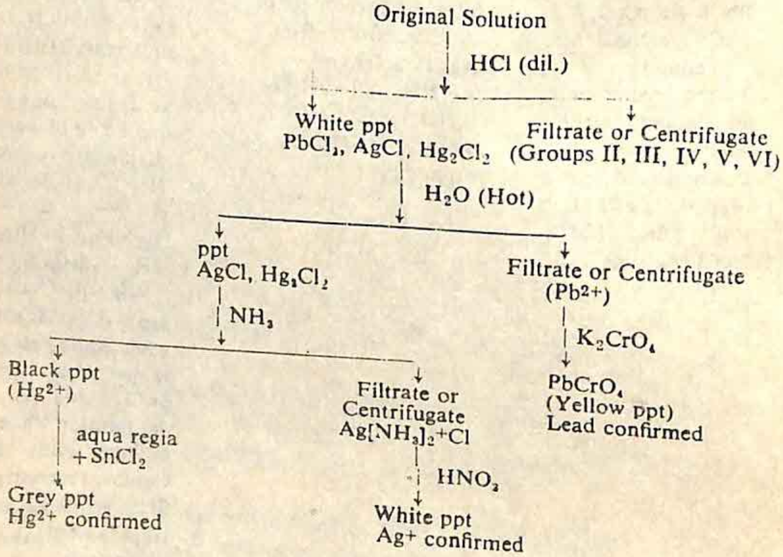
few drops of NH_4OH solution for neutralisation and then add KI solution dropwise. Formation of scarlet brown precipitate of HgI_2 confirm Mercury. To this now add excess of KI solution. The precipitate dissolved to give a clear solution of K_2HgI_4.

$HgCl_2+2KI \rightarrow HgI_2+2KCl$

$2KI+HgI_2 \rightarrow K_2HgI_4$ (Scarlet)

FLOW SHEET I

Analysis of Cations of Group I



Systematic Analysis of Group-II Cations

Filterate or centrifugate detained after the filteration of precipitate of group-I contains cations of subsequent groups. From these, the cations of group-II can be precipitated by passing H_2S gas in the hydrochloric acid medium, when precipitate of IInd group cations are obtained as sulphides of HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_5, Sb_2S_5 and SnS_2. As this group consists of large number of cations and causes some difficulty in their identifications we make use of reaction, on the basis of which these cations are further devided into two subgroups, group A and group B.

Precipitation of Second group cations. The filtrate or centrifugate obtained after group I, is warmed slightly. Pass H_2S gas to about 1ml of the solution. If any coloured precipitate is obtained, indicates the presence of IInd group and if white or dirty white precipitate is obtained this shows absence of IInd group cations to the given sample.

In case, a coloured precipitate is formed in the above test, then pass H_2S gas into whole of the solution till the precipitation is complete. Filter or centrifuge and keep the filterate or centrifugate for the precipitation of cation of subsequent groups. Wash this with cold water.

To the precipitate of IInd group in a test tube, add about 5ml of 3M KOH solution or yellow ammoniumsulphide solution, and warm the contents of the tube for 2-3 minutes. Filter or centrifuge. The residue left on the filter paper consists of group II-A and the filtrate may contain the cations of group II-B.

Identify the cation of group II-A and II-B from the residue by referring to Table 4.9 and Table 4.10 and flow sheet II.

If nitric acid is present, in the solution then on passing H_2S along with the sulphides of group-II, some sulphur will also be precipitated due to the oxidation of H_2S by nitric acid. Use of nitric acid should therefore be avoided as far as possible and if it is absolutely necessary, it should be neutralised and the following procedure may be followed:

When O.S. is prepared in HNO_3, then to the filtrate or centrifugate obtained after the separation of group-I cation NaOH solution is added dropwise till a little turbidity is obtained. Add excess of dil. HCl to make the solution clear and acidic in respect of hydrochloric acid. Test for cations of subsequent groups.

TABLE 4.9

Scheme for the analysis of group II-A (HgS, PbS, Bi_2S_3, CuS, CdS)

<table>
<tr><td colspan="3">The residue of group II-A detained, is washed 2-3 times with cold water on the filter paper in test-tube. Take the residue after washing, in a test tube, add 4-5ml of dil. HNO_3 and heat to boil. Filter or centrifuge.</td></tr>
<tr><td rowspan="4">Residue: (HgS Black) Dissolve the residue in minimum amount of aqua regia. Dilute it by adding 2-3ml of water. Divide into two parts
(1) To one part, add $SnCl_2$ solution dropwise when white precipitate turning black confirms mercury.
$HgCl_2+SnCl_2 \rightarrow Hg_2Cl_2+SnCl_4$
$Hg_2Cl_2+SnCl_2 \rightarrow SnCl_4+Hg$
(2) To the other part add few drops of KI solution. Brown Coloured precipitate soluble in excess of KI confirms mercury.</td><td colspan="2">Filtrate or centrifugate may contain nitrates of Pb, Bi, Cu and Cd. Add about 1-2ml of dil. H_2SO_4 heat and add few drops of ethyl alcohol. Stir the solution and allow to stand for some time. Filter or centrifuge.</td></tr>
<tr><td>Residue $PbSO_4$ (White) Dissolve the residue in about 2ml of glacial acetic acid and ammonium acetate mixture. Divide into two parts:
(1) To one part, add KI solution. Formation of yellow precipitate confirms lead.
(2) To the other part add few drops of K_2CrO_4 solution. Formation of yellow precipitate of $PbCrO_4$ confirms lead.</td><td>Filterate or centrifugate may contain the cations of Bismuth, copper and cadmium, add slight excess of NH_4OH Residue: $Bi(OH)_3$ (White) Dissolve the residue in minimum amount of conc. HCl. Divide into two parts:
(1) To one part, add excess of water. Formation of white turbidity of BiOCl confirms Bismuth.
$BiCl_3+H_2O \rightarrow BiOCl+2HCl$</td></tr>
<tr><td colspan="2">Filterate or centrifugate may contain copper and cadmium as $Cu(NH_3)_4^{2+}$ and $Cd(NH_3)_4^{2+}$ (if the colour of the filtrate or centrifugate is blue, copper is present otherwise it should be taken as absent). Add slight excess of NaOH solution and filter.</td></tr>
<tr><td>Residue $Cd(OH)_2$ (White) Dissolve the residue in about 1ml of dil. HCl and dilute with about 5ml of water. Pass H_2S gas into the solution. Formation of yellow precipitate of CdS confirms cadmium.
$CdCl_2+H_2S \rightarrow CdS+2HCl$
(Yellow ppt)</td><td>Filterate or centrifugate if blue may contain copper which may be confirmed as follows:
1. To about 1ml of the filtrate, add few drops of acetic acid and 4-5 drops of potassium ferrocyanide $K_4[Fe(CN)_6]$ is added. Formation</td></tr>
</table>

	of reddish brown precipitate confirms copper $2CuSO_4 + K_4[Fe(CN)_6] \rightarrow Cu_2[Fe(CN)_6] + 2K_2SO_4$

TABLE 4.10

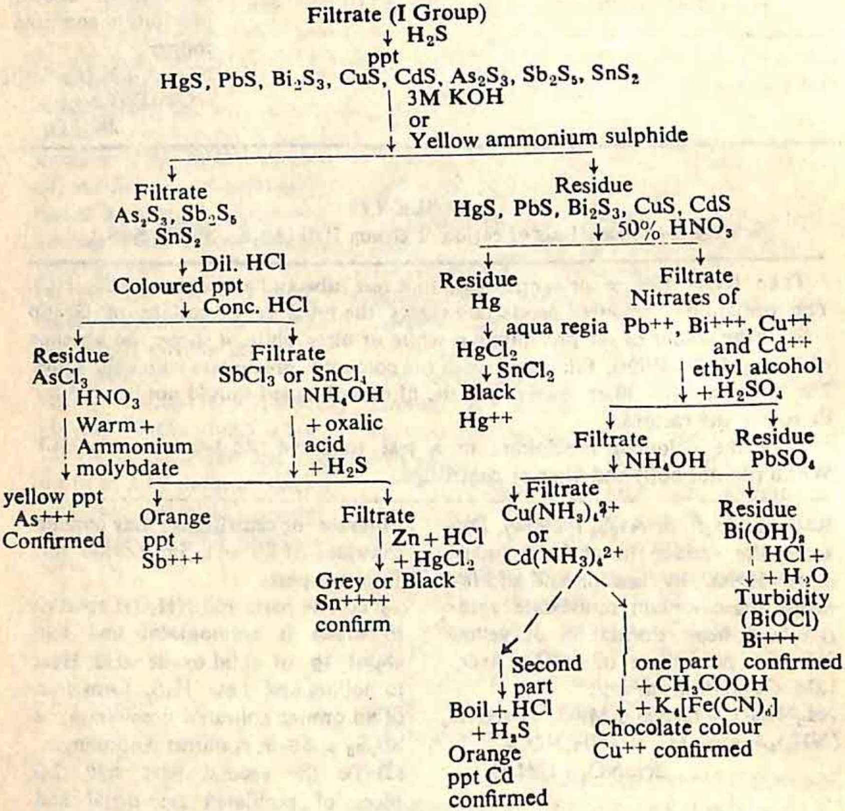
Scheme for the analysis of cation of Group II-B (As_2S_5, Sb_2S_5, SnS_2)

Take KOH filtrate or centrifugate in a test tube and add excess of dil, HCl. The formation of coloured precipitate shows the presence of cations of Group II-B. If the colour of the precipitate is white or dirty white, it shows the absence of Group II-B cations. Filter and wash the coloured precipitate with cold water 2-3 times on the filter paper and the filtrate obtained should not be used for detecting any cations.

Take the coloured precipitate in a test tube and add 3-4ml of conc. HCl. Warm (do not boil) and filter or centrifuge.

Residue: As_2S_5 or As_2S_3 (yellow). Dissolve the residue in about 1-2ml of conc. HNO_3 by heating and add few drops of ammonium molybdate solution and heat. Formation of yellow coloured precipitate of $(NH_4)_3.AsO_4.12MoO_3$ confirms arsenic. $Na_3HAsO_4 + 12(NH_4)_2MoO_4 + 24HNO_3 \rightarrow (NH_4)_3AsMo_{12}O_{40} + 21NH_4NO_3 + 2NaNO_3 + 12H_2O$	Filterate or centrifugate may contain chlorides of Sb and Sn Divide this into two parts: (1) To one part, add NH_4OH solution to make it ammoniacal and add about 1g of solid oxalic acid. Heat to boiling and pass H_2S, formation of an orange coloured precipitate of Sb_2S_3 & Sb_2S_5 confirms Antimony. (2) To the second part, add 2-3 pieces of granulated zinc metal and allow the reaction to complete. Filter and divide into two parts: (a) To one part add $HgCl_2$ solution, when white precipitate turning grey or black confirms tin. (b) To the other part, add NH_4OH solution followed by 1ml of ammonium molybdate solution. Formation of blue colour, confirms tin.

FLOW SHEET II GROUP CATIONS



Systematic Analysis of Group-III cations

$Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$ and some $MnO_2.XH_2O$

The filtrate or centrifugate obtained after the separation of Group-II cations is taken in a boiling tube, and 3-4ml of con. HNO_3 is added. The solution is heated to the boiling stage and the volume of solution is reduced to about 10ml by heating. The advantage of adding conc. nitric acid to the solution is, that it oxidises any excess of H_2S gas dissolved in it and if ferrous ion is present, it gets oxidised to ferric iron.

(The purpose of reducing the volume of the solution to about 10ml is that concentration of cations present increases, which helps in their easier precipitation).

To the solution obtained by the above treatment, add 2-3gms of solid NH_4Cl and *excess of* (1:1) NH_3 solution till the solution smells of ammonia. Formation of gelatin precipitate shows the presence of cations of Group-III as their hydroxides. Filter or centrifuge and retain the filtrate for the identification of cations of subsequent groups. Wash the precipitate with water (2-3ml) two to three times. The confirmation of cations of Group-III is done by referring Table-4.10.

Removal of interfering acid radicals. In the presence of certain anions such as oxalate, tartrate, fluoride, borate and phosphate it is not possible to separate the Group-III Cations from those of the remaining groups by the addition of the group reagents, NH_4Cl and NH_4OH. Before III group, they do not interfere due to the presence of strong acid HCl in which all these anions are highly soluble. Presence of one or more of these interfering acid radicals results in the premature precipitation of the cations of groups IV, V and VI along with III group cations, but disolve in acid solution. Hence, it is evident that these interfering redicals, if present, must be destroyed or eliminated before proceeding with the analysis after third group. Upto II group the medium is acidic so all these anions are soluble in the form of their acids respectively.

$$C_2O_4^{2-} + 2H^+ \longrightarrow \underset{\text{(Oxalic acid)}}{H_2C_2O_4}$$

$$PO_4^{3-} + 3H^+ \longrightarrow \underset{\text{(Phosphoric acid)}}{H_3PO_4}$$

$$F^- + H^+ \longrightarrow \underset{\text{(Hydrofluoric acid)}}{HF}$$

$$BO_3^{3-} + 3H^+ \longrightarrow \underset{\text{(Boric acid)}}{H_3BO_3}$$

In III group the solution is made alkaline by adding NH_4OH, which on ionisation produce hydroxide ion.

$$NH_4OH \longrightarrow NH_4^+ + OH^-$$

$$H_2C_2O_4 + 2NH_4OH \longrightarrow C_2O_4^{2-} + 2H_2O + 2NH_4^+$$

The removal of H^+ ions of weak acids by NH_4OH causes these acids to ionise more and more and thereby the concentration of the interefering ions is increase to such extent that the ionic product (Matellic ion) × (Interefering ion) exceeds the solubility product of their salts. So these anions also get precipitated in group III.

The cids are removed in the following order:

1. *Organic acids*. The filtrate from group II is evaporated to dryness, when organic acid decompose to CO_2 and water. By repeated evapo-

ration with concentrated HNO_3, the residue is completely oxidised. Finally, extract the residue with hot concentrated HCl and then dilute with water.

$$2NO_3^- + 2H^+ + H_2C_2O_4 \rightarrow 2CO_2 + 2H_2O + 2NO_2$$

Borate and fluoride. The filtrate from group II is evaporated to dryness. The residue is repeatedly evaporated almost to dryness in conc. HCl. Finally, extract the residue with hot conc. HCl and dilute it with water.

$$F^- + H^+ \longrightarrow \underset{\text{(Volatile with HCl)}}{HF}$$

$$B_4O_7^{2-} + 5H_2O + 2H^+ \longrightarrow \underset{\text{(Volatile with steam)}}{4H_3BO_3}$$

If borate is present and fluoride is absent, the former may be removed by repeated evaporation to dryness on a water-bath with mixture of 5ml of ethyl alcohol and 10ml of conc. HCl.

$$B_4O_7^{2-} + 12C_2H_5OH + 2H^+ \longrightarrow \underset{\substack{\text{(ethyl borate)} \\ \text{Poisonous}}}{4(C_2H_5)_3BO_3} + 7H_2O$$

Phosphate: (I) *Acetate-Buffer-$FeCl_3$ method*. Dissolve the ppt. produced by the addition of NH_4Cl and NH_4OH in the minimum volume of dil. HCl (the ppt. may contain $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$, $MnO_2 . xH_2O$, traces of CaF_2 and the phosphatesof Mg and of group IIA, IIB, and IV metals. Test for Fe by the addition of $K_4[Fe(CN)_6]$ or KCNS solution. Add NH_4OH to the solution until the solution is alkaline or a faint permanent ppt. is just obtained. Now add 2-3ml of dil. CH_3COOH (1:1) and 10ml of 3N CH_3COONH_4 solution.

Discard any ppt. which may be formed at this stage. If the solution is red, sufficient ferric ion is present. If the solution is not red in

TABLE 4.11
Ferric Chloride Method

Residue: It may contain phosphates of Fe, Al and Cr and also $Fe(OH)_3$. Transfer the ppt into a porcelain dish by means of 10ml of cold water, add 5ml of NaOH solution and 5ml of 30% H_2O_2 solution and boil gently. Filter and wash the ppt. with hot water.		*Filtrate or centrifugate*. Boil down in an evaporating dish to 20-25ml. Add 0.5g of NH_4Cl and NH_4OH solution in slight excess. Filter if necessary.	
Residue	*Filtrate*	*Residue*	*Filtrate*
$FePO_4 + Fe(OH)_3$	Test for Al and Cr.	Test for Al and Cr.	Proceed for IV Group.

colour, add neutral $FeCl_3$ solution drop by drop with stirring, until the solution becomes brownish red in colour. Dilute the solution to about 150ml with hot water, boil gently for 1-2 minutes, filter hot and wash the residue with a little boiling water Table 4.11.

(*II*) *Zirconium nitrate method*. Take the filtrate or centrifugate of II group and boil it to remove H_2S gas. Add 2-3 drops of conc. HNO_3 boil and add 10ml of zirconium nitrate solution. Boil it again. Cool and filter or centrifuge and then add one drop of zirconium nitrate to ensure complete precipitation. Table 4.11

TABLE 4.12

Zirconium Nitrate Method

Residue.	*Filtrate or Centrifugate.*	
Zirconium phosphate, reject	Add solid NH_4Cl and NH_4OH solution and filter.	
	Residue	*Filtrate*
	Test for III group.	Reserve for IV group cations.

SCHEME FOR ANALYSIS OF CATION OF GROUP-III $Fe(OH)_3$, $MnO_2.xH_2O$, $Al(OH)_3$ and $Cr(OH)_3$.

The precipitate formed by the addition of NH_4Cl and NH_4OH solution may contain $Fe(OH)_3$, $MnO_2.xH_2O$, $Al(OH)_3$ and $Cr(OH)_3$, wash the precipitate with a little hot NH_4Cl solution. Take the precipitate in a boiling tube and add about 5-7ml of NaOH and 3-5ml of H_2O_2 solution. Boil gently till the effervescene ceases Table 4.13.

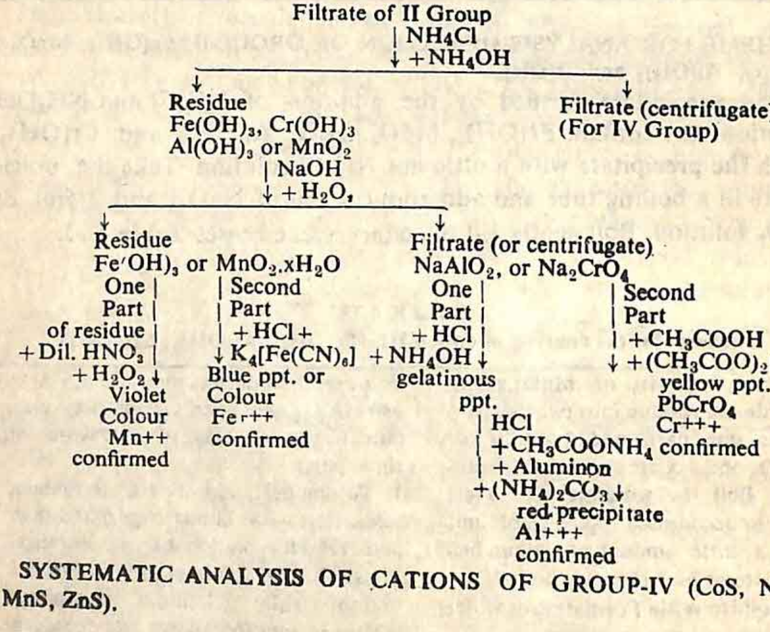
TABLE 4.13

Scheme for the analysis of Group-III. ($Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$)

Residue. $Fe(OH)_3$ or $MnO_2.xH_2O$.	*Filtrate.* If colourless may contain Al^{+++} as $NaAlO_2$ and when yellow may contain Cr^{+++} as Na_2CrO_4. Divide into three parts.
Divide the residue into two parts: 1. To one part, add 1-2ml of dil. HNO_3 and 4-5 drops of H_2O_2 solution. Boil the solution of the test tube to decompose H_2O_2. Cool and add a little amount of sodium bismuthate or lead peroxide and allow the solid to settle. Formation of violet colour confirms manganese. 2. To the other part of the residue, add 2ml of dil. HCl and warm. Divide into two parts.	1. To one part, add dil. HCl to make it acidic (test with litmus paper) and then add NH_4OH solution till the solution is just alkaline and heat to boil. Formation of white gelatinous precipitate floating in solution shows the presence of Al. Filter. HCl $NaAlO_2+H_2O+NH_4OH \longrightarrow NaCl$ $Al(OH)_2+NH_3$

(*a*) To the one part, add few drops of KCNS solution. Formation of blood-red colour confirms iron. $FeCl_3+3KCNS \rightarrow Fe(CNS)_3+3KCl$ (Red)	Take the precipitate in a test tube, add dil HCl to dissolve it. Add 1-2ml of ammonium acetate solution and 0.5ml of Aluminon reagent. Stir and add $(NH_4)_2CO_3$ solution. Formation of red precipitate confirms aluminium.
(*b*) To the other part, add few drops of potassium ferrocyanide solution, $K_4[Fe(CN)_6]$. Formation of the blue precipitate or blue colour confirms iron. $4FeCl_3+3K_4[Fe(CN)_6] \rightarrow Fe_4[Fe(CN)_6]_3 + 12KCl$ (Blue)	2. To the other part, add slight excess of acetic acid and add lead acetate solution. Formation of yellow precipitate of $PbCrO_4$ confirms chromium. $Na_2CrO_4+(CH_3COO)_2Pb \rightarrow PbCrO_4+2CH_3COONa$ (Yellow)
	3. To the other part, add 1-2ml of dilute HNO_3. Cool add 1ml amyl alcohol and 4-5 drops of H_2O_2 solution. Allow the two layers to separate. Blue colour in organic layer confirms chromium.

FLOW SHEET No. III
III GROUP



SYSTEMATIC ANALYSIS OF CATIONS OF GROUP-IV (CoS, NiS, MnS, ZnS).

Take in a boiling tube, the filtrate or centrifugate obtained after the separation of precipitate of Group-III and pass H_2S gas in ammoniacal medium. The filtrate or centrifugate should give smell of NH_3, till no more precipitation occurs. The precipitate if formed, consists, of sulphides of Cobalt, Nickel, Manganese and Zinc as CoS, NiS, MnS, ZnS. Filter, retain the filtrate for the separation of cations of Group-V. Wash the precipitate over the filter paper with water and reject the washing. For the identification of cations of Group-IV, refer to Table 4.14 and flow sheet No. IV.

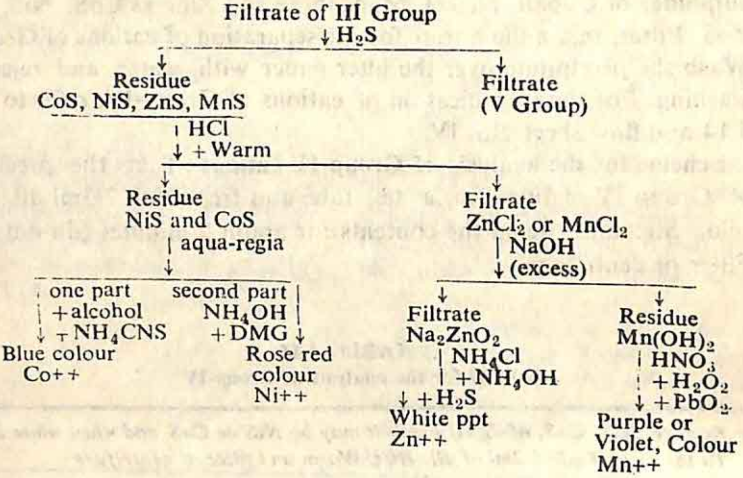
Scheme for the analysis of Group-IV cations. Take the precipitate of Group-IV cations in a test tube and treat with 2-3ml dil. acetic acid. Stir and warm the contents for about 2 minutes (do not boil). Filter or centrifuge.

TABLE 4.14

Scheme for the analysis of Group-IV

Residue: NiS, CoS, MnS, (if black it may be NiS or CoS and when white ZnS). To the residue add 1-2ml of dil. HCl. Warm and filter or centrifuge		
Residue. NiS, CoS (Black)	*Filtrate.* Add NaOH is excess and boil. Filter or Centrifuge	
Dissolve the residue in minimum amount of aqua-ragia (HCl:HNO_3 3:1) and dilute it by adding about 2-3ml of water. Divide into two portions: 1. To one part, add 1ml of alcohol, 0.5-1gm of ammonium thiocyanate (NH_4SCN) and stir the solution. Formation of a blue colour in organic layer confirms Cobalt. 2. To the other part, add NH_4OH to make it ammonical and add 4-5 drops of Dimethyl glyoxime reagent. Rose-red coloured precipitate confirms Nickel. $NiCl_2 + 2NH_4OH + 2C_4H_8N_2O_2 \rightarrow 2NH_4Cl + Ni(C_4H_7N_2O_2)_2 + 2H_2O$ (Red)	Filtrate or centrifugate may contain Zinc and confirm its presence as under: 1. To one part of the solution, add solid NH_4Cl and NH_4OH solution till it smells of NH_3. Pass H_2S gas. White precipitate of ZnS confirms Zinc $Na_2ZnO_2 + H_2S \rightarrow ZnS + 2NaOH$ (white) ppt. 2. To the other part of the solution add 1% Dithiozone solution (in CCl_4). a rose red colour is formed which changes into green on the addition of 1 or 2 drops of dil. HCl.	Residue may contain manganese. To the filtrate or centrifugate, add 1ml of dil. HNO_3 and 3-4 drops of H_2O_2. Heat to boil and add a small amount of solid sodium bismuthate or solid PbO_2. Allow the solid to settle when a purple or violet colour formation, due to permanganate confirms Manganese. $Mn(OH)_2 + 2HNO_3 \rightarrow Mn(NO_3)_2 + 2H_2O$. $Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \rightarrow 5Pb(NO_3)_2 + 2KMnO_4 + 2H_2O$ (Pink)

FLOW SHEET No. IV
IV GROUP



Systematic analysis of cations of Group-V (Ba, Ca & Sr)

The filtrate obtained after the separation of cation Group-IV may contain cations of Group-V and Magnesium (Group-VI). From this the cations of group V, Ba^{2+}, Sr^{2+}, Ca^{2+} can be precipitated as their insoluble carbonates after removing H_2S gas from it. The procedure given below may be followed.

The filtrate or centrifugate is boiled for some time and the volume of the solution is reduced to about 5ml. This is made ammonical by adding 1-2gm of solid NH_4Cl and a few ml of NH_4OH. To this add 4-5ml of saturated solution of ammonium carbonate. Formation of white precipitate shows the presence of Group-V cations, filter and keep the filtrate for the identification of Magnesium. Wash the precipitate over the filter paper with 3-4ml of cold water and consult Table 4.15, for the systematic detection of cations of Group-V and flow sheet No. V.

$$MCl_2 + (NH_4)_2CO_3 \rightarrow MCO_3 + 2NH_4Cl \quad (M = Ba, Sr, Ca)$$

Scheme for the analysis of cations of group-V. Dissolve the precipitate in 3-4ml of dil acetic acid and warm if necessary. Test for the presence of Barium in the solution by taking few drops of the above solution and adding to it few drops of K_2CrO_4 solution. If yellow coloured precipitate is detained, then add K_2CrO_4 solution to whole of the solution Table 4.15.

$$(CH_3COO)_2Ba + K_2CrO_4 \rightarrow \underset{\text{(Yellow)}}{BaCrO_4} + 2CH_3COOK$$

If no yellow coloured precipitate is obtained, Barium is taken to be absent. Filter or centrifuge if yellow coloured precipitate is obtained.

TABLE 4.15

Scheme for the analysis of Group V

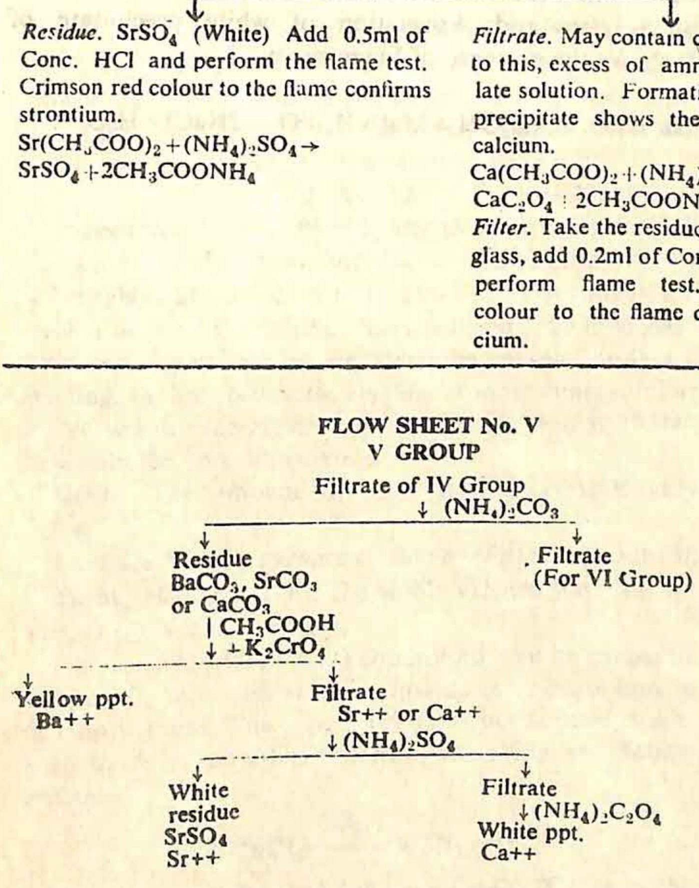
Residue.)$BaCrO_4$ (Yellow) Dissolve in minimum amount of Conc. HCl and perform the flame test. Grassy green flame confirms Barium.	*Filtrate or centrifugate may contain.* Strontium and calcium. Add excess of Ammonium sulphate solution.

Filter after warming.

Residue. $SrSO_4$ (White) Add 0.5ml of Conc. HCl and perform the flame test. Crimson red colour to the flame confirms strontium. $Sr(CH_3COO)_2 + (NH_4)_2SO_4 \rightarrow SrSO_4 + 2CH_3COONH_4$	*Filtrate.* May contain calcium. Add to this, excess of ammonium oxalate solution. Formation of white precipitate shows the presence of calcium. $Ca(CH_3COO)_2 + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4 + 2CH_3COONH_4$ *Filter.* Take the residue, on a watch glass, add 0.2ml of Conc. HCl and perform flame test. Brick red colour to the flame confirms Calcium.

FLOW SHEET No. V

V GROUP



Procedure for confirmation of Magnesium. The filtrate or centrifugate from Group-V may contain Mg, Na, K and ammonium salts and out of these only Magnesium is identified here as the salts of other cations have been added in the schematic analysis of various groups at different stages. The following procedure may be followed for confirming Magnesium.

The above filtrate or centrifugate is heated to dryness. The dry mass obtained is further heated strongly in a fumes-cupboard for sometime to decompose ammonium salts. Cool and add to this 2-3 ml of dil. HCl and heat for some time. Cool and filter if necessary.

To 1ml of the solution, add few drops of Na_2HPO_4 and add NH_4OH till the solution smells of ammonia. Scratch the inner sides of the tube with a glass rod. Formation of white precipitate of $Mg(NH_4)PO_4$ shows the presence of Magnesium.

$$MgCl_2 + Na_2HPO_4 + NH_4OH \rightarrow Mg(NH_4)PO_4 + 2NaCl + H_2O$$

5

Inorganic Preparations

Exercise 5.1. *To prepare the crystals of monoclinic sulphur.*

Theory. The crystals of monoclinic sulphur are obtained when powdered sulphur is dissolved in xylene and then allowed to cool. Long prismatic crystals of monoclinic sulphur are obtained.

Chemicals required. 1. Powdered sulphur=10g
2. Xylene =20.0ml.

Procedure. Take 20ml of xylene in a hard glass test tube; add to this 1.0 gm of powdered sulphur. Close the test tube with a stopper having a long glass tube attached to it. Hold this test tube in a ring stand and heat it until all the sulphur has dissolved. The long glass tube helps to condense the xylene vapour. Filter the hot solution in a china dish. On cooling, the long prismatic crystals of monoclinic sulphur are obtained. Filter and dry the crystals. Determine the weight of the crystals and calculate the percentage yield.

Result. The amount of pure sulphur crystals should be about 2.0 g.

Exercise 5.2. *To prepare a sample of pure cuprous chloride* (Cu_2Cl_2).

Theory. Copper (*II*) is the stable valence state of copper whereas copper (*I*) is not so stable.

Cuprous chloride, Cu (*I*) compound, can be prepared by reducing copper (*II*) ions with sulphur dioxide or sulphite ions in the presence of chloride ions. The copper (*I*) ions once formed, react with chloride ions to form cuprous chloride according the following chemical reaction:

$$2\,CuCl_2 \xrightarrow{SO_2} Cu_2Cl_2 + Cl_2$$

$$2\,Cu^+ + 2\,Cl^- \longrightarrow Cu_2Cl_2 \text{ (Cuprous chloride)}$$

Cuprous chloride can be prepared by any one of the following methods:

Method I.

Chemicals required. *1.* Sodium Sulphite Na_2SO_3 = 2.5g,

2. Cupric Chloride = 3.25g;

3. Sulphurous acid (H_2SO_3) solution, (10g Na_2SO_3 in one litre of water and add 10ml dil. HCl);

4. Glacial acetic acid = 2.5ml;

5. Ether = 7.5ml.

Procedure. Dissolve 2.5g of sodium sulphite in 25ml of water to obtain sodium sulphite solution. Sulphurous acid solution can be prepared by dissolving 10g of sodium sulphite in one litre of water containing 10ml of dilute HCl.

Dissolve 3.25g copper (*II*) chloride in 6ml water and then add slowly the sodium sulphite solution with constant stirring. Dilute the suspension of cuprous chloride formed with 200ml of sulphurous acid solution and allow the precipitate to settle down. Decant off the supernatant liquid. Filter the white solid under suction and wash the precipitate with sulphurous acid solution. Finally wash the precipitate with glacial acetic acid and ether. Dry the product, transfer it to a test tube and stopper it well so that the copper (*I*) chloride does not oxidise into copper (*II*) chloride.

Method II.

Cuprous chloride can also be prepared by heating copper (*II*) sulphate with hydrochloric acid and copper turnings.

$$CuSO_4 + 2HCl + Cu \longrightarrow \underset{\text{(Cuprous chloride)}}{Cu_2Cl_2} + H_2SO_4$$

Chemicals required. *1.* Copper sulphate ($CuSO_4.5H_2O$) = 5g;

2. Sodium chloride (NaCl) = 2.5g;

3. Copper turnings = 2.5g;

4. Hydrochloric acid (HCl) = 7ml;

5. Sodium sulphite = 2.0g;

6. Alcohol = 20ml.

Procedure. Place cupric sulphate, sodium chloride, copper turnings and conc. HCl in a 100ml round bottom flask. Cover the mouth of the flask with a funnel and heat the mixture until greenish blue colour of the cupric ions had disappeared. Pour the colourless contents of the flask into a beaker containing about 150ml water to which about 2g of sodium sulphite has previously been added. A white precipitate of cuprous chloride (Cu_2Cl_2) is formed, which is filtered under suction. Wash the precipitate with sodium sulphite solution and finally, with alcohol followed by ether. Dry the sample in an oven.

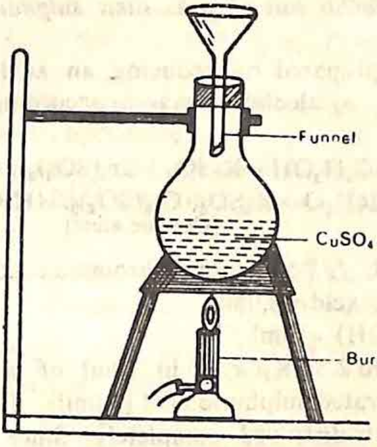


FIG. 5.1 Preparation of Cuprous Chloride.

Exercise 5.3. *To prepare a pure sample of cuprammonium sulphate tetrahydrate or tetramine cupric sulphate tetrahydrate,* $[Cu(NH_3)_4]SO_4.4H_2O$.

Theory. When excess of ammonia is added to a solution of cupric sulphate, deep blue solution of cuprammonium sulphate complex results. The complex salt is reprecipitated from the solution by the addition of alcohol in which it is insoluble. The chemical reation can be written as:

$$CuSO_4 + 4NH_4OH \longrightarrow \underset{\text{(Tetraminecupric Sulphate tetrahydrate)}}{Cu[(NH_3)_4]SO_4.4H_2O}$$

Chemicals required. *1.* Copper sulphate = 2.5g;

2. Concentrated ammonia (1:1) = 5.0ml;

3. Alcohol = 10.0ml.

Procedure. Dissolve the requisite amount of copper sulphate (2.5g) in about 10ml of water, in a 100ml beaker. Add concentrated ammonia solution to it until a clear blue solution is obtained. If turbidity still persists, add more of ammonia solution. Now add dropwise 10ml alcohol, with constant stirring when a purple precipitate of cuprammonium sulphate is obtained. Heat the beaker to about 50°C on a water bath for 10-15 minutes to dissolve the precipitate. Allow it to cool to get the blue coloured crystals. Filter and wash them with alcohol. Dry, record the yield and calculate the percentage yield.

Exercise 5.4. *To prepare the crystals of chrome alum ($K_2SO_4.Cr_2(SO_4)_3.24H_2O$)*

Chrome alum is a double salt of potassium sulphate and chromium sulphate.

Theory. It can be prepared by reducing an acidified solution of potassium dichromate by alcohol or starch, according to the following chemical reaction:

$$K_2Cr_2O_7+4H_2SO_4+3C_2H_5OH \rightarrow K_2SO_4+Cr_2(SO_4)_3+3CH_3CHO+7H_2O$$

$$K_2SO_4+Cr_2(SO_4)_3+24H_2O \rightarrow \underset{\text{(Chrome alum)}}{K_2SO_4.\ Cr_2(SO_4)_3.24H_2O}$$

Chemicals required. *1.* Potassium dichromate = 2.5g;

2. Conc. Sulphuric acid = 2.0ml;

3. Alcohol (C_2H_5OH) = 10ml.

Procedure. Dissolve 2.5g $K_2Cr_2O_7$ in 10ml of water in a 100ml beaker. Add concentrated sulphuric acid (2.0ml) dropwise and stirr until the dichromate is dissolved completely. Since heat is evolved during dissolution, cool the solution to about 30°C by placing the beaker in an ice bath. Now add ethyl alcohol (10ml) dropwise, with constant stirring. The temperature should not be allowed to exceed 50°C, and a few pieces of ice may be added to the solution, to maintain this temperature. Allow the contents to stand overnight. Seperate the violet coloured crystals from the mother liquor, dry them by pressing between the filter paper and weigh. Record the yield and calculate percentage yield of the product.

Exercise 5.5. *To prepare the crystals of potassium trioxalto Chromate (III) $K_3[Cr(C_2O_4)_3]3H_2O$.*

Theory. When potassium dichromate is treated with oxalic acid and potassium oxalate, a green complex of potassium trioxalatochromate (III) is formed, according to the following chemical equation:

$$2K_2C_2O_4+7C_2H_2O_4+K_2Cr_2O_7 \longrightarrow \underset{\text{[Potassium Trioxalato Chromate (III)]}}{2K_3[Cr(C_2O_4)_3]}+6CO_2+7H_2O$$

Chemicals required. *1.* Potassium oxalate (Monohydrate) = 1.5g;

2. Oxalic acid (dihydrate) = 3.5g;

3. Potassium dichromate = 1.3g;

4. Acetone = 5ml.

Procedure. Dissolve potassium oxalate (1.5g) and oxalic acid (3.5g) in water (50ml) in a 100ml conical flask. Add potassium dichromate (1.3g) slowly (a pinch at a time) with vigorous stirring. When the reaction is complete, evaporate the solution to nearly one third of its original volume and allow to stand overnight when green coloured crystals are obtained. Filter the product under suction, wash with acetone and dry. Record the yield and calculate the percentage yield.

Exercise 5.6. *To prepare a sample of Potassium Permanganate,* $KMnO_4$.

Theory. Potassium permanganate is prepared by fusing manganese dioxide with potassium hydroxide in presence of an oxidising agent like $KClO_3$ when potassium manganate is formed. This when treated with carbon dioxide yields potassium permanganate, according to the following reactions:

$$6KOH + 3MnO_2 + KClO_3 \longrightarrow 3K_2MnO_4 + KCl + 3H_2O$$

$$3K_2MnO_4 + 2CO_2 \longrightarrow 2KMnO_4 + 2K_2CO_3 + MnO_2$$

Chemicals required. *1.* Manganese dioxide = 3.5g;

2. Potassium hydroxide = 4.0g;

3. Potassium chlorate = 2.0g.

Procedure. A mixture of potassium hydroxide (4.0g) and potassium chlorate (2.0g) is melted in an iron dish, which is clamped strongly on a tripod stand. Finely powdered manganese dioxide is then added slowly (a pinch at a time) and the mixture is stirred vigorously with an iron rod, and heated (not strongly) to maintain it in a molten condition. Cool the mixture and powder it, in a mortar. Boil gently for about 1.50 hrs. with 100ml. water in a 500ml pyrex beaker.

Pass carbon dioxide gas through the water solution till a drop of the solution, when placed on a filter paper, does not give green colour. The solid matter is then allowed to settle for about 10 minutes and the clear upper liquid is then filtered through a thick plug of glass wool in a funnel. The solution is evaporated in a porcelain dish till crystallization commences. Filter the crystals of potassium permanganate, dry them on a filter paper. Weigh and record the yield and calculate the percentage of yield of the product.

Exercise 5.7. *To prepare the crystals of potash alum,* $K_2SO_4.Al_2(SO_4)_3.24H_2O$.

Theory. Potash alum is commonly known as 'alum' is a double salt of potassium sulphate and aluminium sulphate.

Potash alum can be obtained by mixing equimolar solution of potassium sulphate and aluminium sulphate according to the following equation:

$$K_2SO_4 + Al_2(SO_4)_3.18H_2O + 6H_2O \longrightarrow \underset{\text{(Potash alum)}}{K_2SO_4.Al_2(SO_4)_3.24H_2O}$$

Chemicals required. *1.* Potassium sulphate (K_2SO_4) =2.0g,

2. Aluminium sulphate=8.0g.

Procedure. Dissolve potassium sulphate (2.0g) and aluminium sulphate (8.0g) separately in minimum quantities of water (10ml water for each) since aluminium sulphate is less soluble in water, its turbid solution can be made clear by warming and adding 3-4 drops of concentrated sulphuric acid. Mix the two solutions in a china dish and leave overnight. Separate the crystals formed from the mother liquor. Dry them at the room temperature and weigh. Record the yield and calculate the percentage yield of the sample.

Exercise 5.8. *To prepare the crystals of ferrous ammonium sulphate (Mohr's Salt)* $FeSO_4\ (NH_4)_2\ SO_4.\ 6H_2O$.

Method I

Theory. It can be prepared by mixing solution of equimolecular quantities of ferrous sulphate and ammonium sulphate and subsequently evaporating the solution to crystallisation, when the double salt seperates out. The chemical reaction can be written as:

$$FeSO_4.7H_2O + (NH_4)_2SO_4 \longrightarrow \underset{\text{(Mohr's Salt)}}{FeSO_4(NH_4)_2SO_4 6H_2O} \quad H_2O$$

Chemicals required. 1. Ferrous sulphate ($FeSO_4.7H_2O$) 7g;

2. Ammonium sulphate 3.5g;

3. Sulphuric acid (dil.) 2ml.

Procedure. Dissolve (7g) ferrous sulphate and ammonium sulphate crystals in 10ml of acidified hot water (at 80-90°C) containing about 2ml of dil. H_2SO_4. Boil the solution for 2-3 minutes and allow the beaker to cool slowly, by placing it in ice cold water. Crystals begin to seperate out, gradually. (The reaction should be carried out in the presence of H_2SO_4 (dil.)otherwise ferrous sulphate will be converted into ferric sulphate by oxidation or it may be hydrolysed, and the solution will become yellow). When the crystallization is complete. Filter and dry between the folds of the filter paper. Weigh the crystals. Record the yield and calculate the percentage yield.

Method II

From iron filings. Mohr's salt can also be prepared by dissolving a known quantity of iron filings in dilute sulphuric acid and adding a calculated amount of ammonium sulphate to the solution. The chemical reaction can be symbolised as under:

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2\uparrow$$

$$FeSO_4 + (NH_4)_2SO_4 + 6H_2O \rightarrow \underset{\text{(Mohr's salt)}}{FeSO_4(NH_4)_2SO_4.6H_4O}$$

Chemicals required. 1. Iron filings = 2.5g;

2. Ammonium sulphate = 5.0g;

3. Sulphuric acid (conc.) = 2.0ml.

Procedure. Add 2ml concentrated sulphuric acid dropwise to 20ml water taken in a conical flask. To this add 2.0g of iron fillings. Heat it on a wire gauge for about 15 minutes. Remove the burner when reaction becomes vigorous (avoid contact of ensuing hydrogen gas with flame). Cool and filter. In the residue add 8ml more of dilute sulphuric acid and repeat the procedure. Collect both the filterate in a 250ml beaker and add to it a saturated solution of 5.0g ammonium sulphate, concentrate the solution by heating to a point when crystallization just begins. Cool the solution for two hours. Filter the crystals, dry, weigh and record percentage yield.

Exercise 5.9. *To prepare the crystals of ferric alum.* $(NH_4)_2SO_4Fe_2(SO_4)_3 24H_2O$.

Theory. Ferric alum. crystals can be prepared by cry tallizing out combined solution of ammonium sulphate and ferric sulphate in the presence of sulphuric acid. Ferric sulphate is obtained by oxidation of ferrous sulphate by mean of nitric acid:

$$2FeSO_4 + 2HNO_3 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2H_2O + 2NO_2\uparrow$$

$$(NH_4)_2SO_4 + Fe_2(SO_4)_3 \xrightarrow{\text{dil. } H_2SO_4} \underset{\text{(Ferric alum)}}{(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O}$$

Chemicals required. 1. Ferrous sulphate heptahydrate = 2.5g;

2. Sulphuric acid (dil.) = 13.0ml;

3. Nitric acid (conc.) = 2.5ml;

4. Ammonium Sulphate = 1.5g.

Procedure. Take ferrous sulphate in 100ml conical flask. Add 13ml of dilute H_2SO_4 and add 15ml water, heat on a boiling water bath or over a low flame. Add conc. HNO_3 in small lots till no more brown vapours are obtained (Nitric acid is added for the oxidation of ferrous ions to ferric ions). Evaporate the solution to nearly dryness and add the given ammonium sulphate along with 25ml of distilled water with constant stirring. If the solution is brown in colour, add a few drops of conc. H_2SO_4 to get pale yellow liquid. Transfer the solution to a china dish and place it in a cool place for few days when yellowish coloured crystals of ferric alum are obtained. Filter the crystals under suction dry them in air and record the yield and calculate the percentage yield.

Exercise. 5.10. *To prepare the crystals of sodium thiosulphate,* $Na_2S_2O_3.5H_2O$.

Theory. Sodium thiosulphate can be prepared, by boiling sodium sulphite solution with excess of finely powdered sulphur, according to the following reaction:

$$Na_2SO_3 + S \xrightarrow{H_2O} Na_2S_2O_3.5H_2O$$

(Sodium Thiosulphate)

Chemicals required. 1. Sodium sulphite = 5.0g; 2. Sulphur = 1.0g.

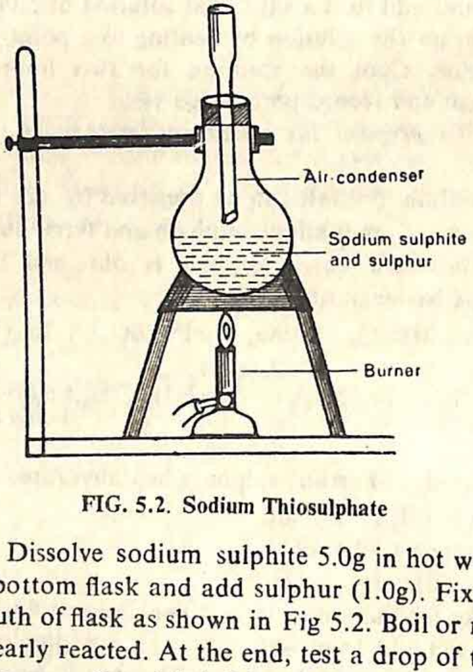


FIG. 5.2. Sodium Thiosulphate

Procedure. Dissolve sodium sulphite 5.0g in hot water (10ml) in a 100ml round bottom flask and add sulphur (1.0g). Fix an air condenser in the mouth of flask as shown in Fig 5.2. Boil or reflux till all the sulphur has nearly reacted. At the end, test a drop of the liquid with a red litmus paper or phenolphthalein which should not turn pink, i.e., the solution should not be alkaline. Add more sulphur if necessary. Filter the solution and concentrate the filtrate to about 25ml, i.e., crystallization point. Then allow it to cool when sodium thiosulphate begins to crystallize. Add 1 or 2 crystal of sodium thiosulphate, which act as nuclei for crystallization. Remove the crystals from the mother liquor, dry them between the folds of filter paper.

Exercise 5.11. *To prepare a sample of prussian blue* $Fe_4[Fe(CN)_6]_3$

Theory. Prussian blue can be prepared by mixing $FeCl_3$ with $K_4[Fe(CN)_6]$. The reaction may be represented as,

$$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{(Prussian blue)}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

Method I

Chemical required. *1.* $FeCl_3$ (anhydrous) = 2g;

2. $K_4[Fe(CN)_6]$ = 4.5g;

Procedure. Dissolve 2g $FeCl_3$ in 2-3ml and 4-5g of $K_4[Fe(CN)_6]$ in distilled water separately. On mixing the two solutions a blue coloured paste is formed. Dry it between the folds of filter paper. Weigh and determine the percentage of yield.

Method II

It can also be prepared from the iron filings. On heating iron filings with dil. H_2SO_4 give $FeSO_4$. This is converted into ferric sulphate by aerial oxidation. When ferric sulphate is mixed with $K_4[Fe(CN)_6]$ solution a blue coloured complex is precipitated out. The reaction may be repersented as:

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2\uparrow$$

$$2FeSO_4 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{(Turnbull's green)}}{Fe_2[Fe(CN)_6]} + 2K_2SO_4$$

$$2Fe_2(SO_4)_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{(Prussian blue)}}{Fe_4[Fe(CN)_6]_3} + 6K_2SO_4$$

Turnbull's green can also be converted into Prussian blue on oxidation.

Chemicals required. 1. Iron filings 0.5g;

2. Ethyl alcohol = 15ml;

3. Sulphuric acid (dil.) = 100ml;

4. $K_4[Fe(CN)_6]$ = 4.5g.

Procedure. Take 0.5g iron filings in a beaker and add 10ml of dil. H_2SO_4. Heat it on a wire gauze for 15 minutes. Remove the burner when reaction becomes vigorous (avoid contact of the ensuing hydrogen gas with flame) cool and filter. To the residue, add 8ml more of dilute sulphuric acid and repeat the procedure. Collect both the filtrates in a 250ml beaker and add to it a saturated solution of 4.5g potassium ferrocynide. Heat the solution till it becomes green. The green coloured product changes to blue on keeping in air for nearly two hours.

The addition of 1-2ml of $K_2Cr_2O_7$ will enhance the oxidation of green product.

Exercise 5.12. *To prepare a pure sample of sodium chloride from commercial common-salt.*

Principle. Pure sample of sodium chloride can be obtained by passing hydrogen chloride gas into a saturated solution of the commercial sample. On adding hydrogen chloride the concentration of chloride ions (Cl^-) increases and this pushes the equilibrium to the right according to the following chemical equation, thus resulting in the precipitation of pure sodium chloride. This is known as commou ion effect.

$$\underset{\substack{\text{solid}\\\text{undissolved}}}{NaCl} \dashrightarrow \underset{\text{(solution)}}{NaCl \rightleftharpoons Na^+ + Cl^-}$$

$$HCl \rightleftharpoons H^+ + Cl^-$$

Chemicals required. (*i*) Impure sample of NaCl

(*ii*) Conc. H_2SO_4

(*iii*) NaCl

Procedure. Fit up an apparatus for the preparation of hydrogen chloride gas (heat: NaCl with conc. sulphuric acid). A saturated solution of the commercial sample of sodium chloride is prepared in hot water. Cool and filter the solution. Pass HCl gas into the solution until the precipitation is complete. Decant off the clear liquid and add a little of distilled water.

Heat on a steam bath to remove the hydrogen chloride gas. Dry the crystals on a porous plate and weigh. Record the weight.

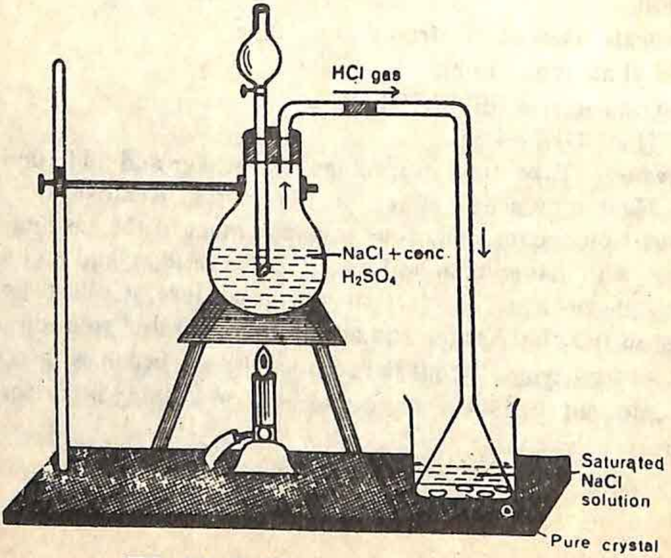


FIG. 5.3. Purification of sodium chloride

6

Crystallization

Since the days of the earliest alchemists, one of the most common and important processes of purification of crystalline organic compounds, that is very frequently employed in practical organic chemistry, is the crystallization from a suitable solvent. The fact, that most of solids are dissolved to a greater extent in suitable solvent at high temperature and maximum amount of the solute is thrown out as crystals, when cooled, constitutes the basic principle of crystallization. The process involves the following steps ·

(1) Choice of a solvent. An ideal crystallization solvent should dissolve a large amount of the substance at its boiling point and only a small amount at the room temperature. The best helpful watchword to meet this requirement is 'like dissolves like'. It should have a low temperature coefficient for impurities and should not react chemically with the solute, and should be perfectly safe to use. Further, on cooling it should readily deposit well formed cystals of the purified compound, from which it should be easily removable. Lastly, it should be inexpensive. The solvents that are frequently used for crystallization are listed in Table 6.1.

TABLE 6.1

Common Crystallization Solvents

Solvent	*Formula*	*Boiling point °C*	*General characteristics*
Water	H_2O	100	Non-flammable, it is usually the solvent of choice, if solubility and crystallization requirements are fulfilled.
95% ethyl alcohol	C_2H_5OH	78	Inflammable, hygroscopic, should be used under dry conditions.

Diethyl ether	$(C_2H_5)_2O$	36.6	Highly inflammable, immiscible with water, should be avoided if possible.
Acetone	CH_3COCH_3	56.1	Highly inflammable, miscible with water.
Benzene	C_6H_6	80.2	Inflammable, immiscible with water, non-toxic in nature.
Chloroform	$CHCl_3$	61.3	Non-inflammable, immiscible with water, vapours possess anaesthetic effect.
Carbon tetrachloride	CCl_4	76.7	Non-inflammable, immiscible with water, vapours are toxic in nature.
Acetic acid	CH_3COOH	118.1	Non readily inflammable, pungent smell, miscible with water.
Methyl alcohol	CH_3OH	64.7	Inflammable, miscible with water, vapours may cause blindness if inhaled for a long time.

(2) **Preparation of the saturaled solution.** After selecting a suitable solvent, the next step is to dissolve the solute in a minimum amount of solvent at the boiling point or slightly below this. For this, finely divided solute is placed in a small beaker of suitable size and a minimum amount of the solvant chosen is added to it. Heat to boiling on a steam-bath (for high boiling solvents, i.e., B. Pt. more than 100°C, hot plate covered with asbestos sheet), constantly stirring the mixture. Add more solvent in small portions with stirring to the boiling solution, continue addition of the solvent, until all the solute has dissolved. If some insoluble impurity is accumulated, decant the solution from the solid material. If during the preparation of solution, it becomes coloured, boil it with a small amount of activated charcoal for 5 to 10 minutes, this will remove the colour.

(3) **Filtration.** This step is done to eliminate insoluble impurities from the saturated solution prepared in step 2. If the solution is perfectly clear, filtration may be omitted. To avoid the premature crystallization of the solute on the filter paper or in the funnel stem before filtration is complete and thereby choking the funnel, the hot solution should be filtered. This usually requires rapid filtration with a minimum of evaporation through a hot water funnel (Fig.6.1).

The funnel should not, however, be heated above the boiling point of the solvent.

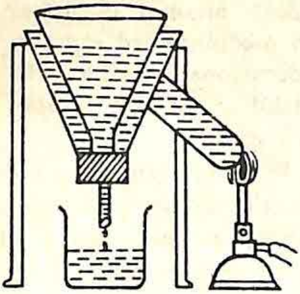


FIG. 6.1. Hot water Funnal.

To increase the rate of filtration, a fluted filter paper (Fig. 6.2) should be used. The folding of a fluted paper may be learnt far more readily by a demostration in the laboratory than by any written description.

(4) **Cooling.** The hot filtered solution is quickly poured into a lipped beaker and covered with a watch-glass to avoid any evaporation. The main purpose of the cooling is to bring about the crystallization of the maximum amount of desired material with a minimum amount of impurity. The size of the crystals is controlled by the rate of cooling, a slow to moderate rate of cooling is usually best as it will favour medium-sized crystals, which are generally

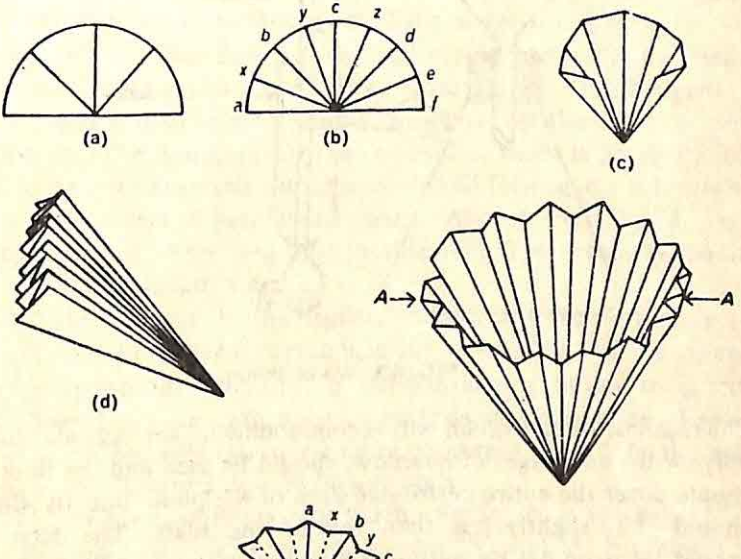


FIG. 6.2. Preparation of a Fluted Filter Paper.

preferred. A slow cooling rate gives large crystals, which are likely to include considerable amounts of solvent carrying impurities with it and complicates the drying process. A rapid rate, on the other hand, favours small crystals, which absorb significant amount of impurities on their large surface area. To obtain medium-sized crystals, the mixture should be allowed to stand with occasional shaking until the crystallization is complete, too long standing of the crystals in contact with the mother liqour should be avoided.

(5) **Collecting and washing the crystals.** When crystallization is complete, the mixture of crystals and crude mother-liquor is filtered with a Buchner funnel fitted by means of a rubber stopper into a clean filter flask connected to a water-pump or vacuum-pump (Fig 6.3)

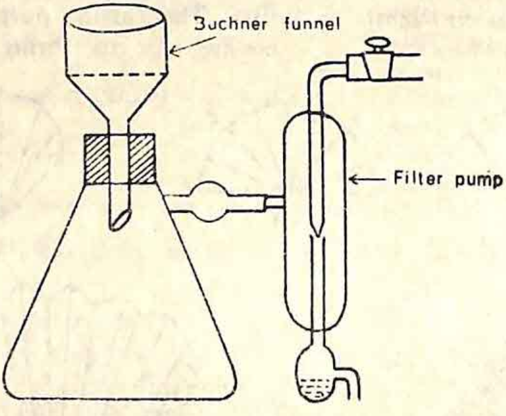


FIG. 6.3. Water Pump.

The smallest funnel which will accommodate all the crystals comfortably with no danger of overflow, should be used and the filter paper should cover the entire perforated area of the plate but its diameter should be slightly less than that of the plate. The filter paper should be made flat by wetting it with solvent and applying suction. The mixture is poured into the funnel and full suction is applied in order to drain the mother-liqour from the crystals as effectively as possible. When the filter-cake is rigid enough it is pressed carefully but firmly by means of a cork or an inverted bottle stopper. When the flow of liquid stops, the suction is discontinued.

The crystals are then washed to remove all the adhering impurities. To accomplish this, the crystals are covered with a small portion of fresh, cold solvent and the mixture is carefully stirred with a spatula or flattened stirring rod to ensure uniform wetting of the crystals. Suction is again applied and crystals are pressed as before. This process may be repeated several times with small protions of cold solvent. Finally, if the solvent is high boiling, an ultimate washing with a small amount of a low-boiling solvent in which the crytals are insoluble or only sparingly soluble may be recommended.

(6) **Drying of the crystals.** The final step of the process is to obtain crystals free from adhering solvent by drying. The Buchner funnel is inverted on to a pad of several thicknesses of coarse-grained smooth surfaced filter paper and a similar pad is placed on the top of crystals and most of the solvent squeezed out by pressing strongly.

The crystals are then transferred to a clean watchglass or crystallizing dish and covered with a sheet of filter-paper to keep out dust particles. The final traces of mother-liquor can then be rapidly removed by drying in a stream of hot air from a heater, such as an ordinary hair drier or in electric oven, if the material is physically stable up to 100°C. The drained material should preferably be dried in a desiccator using calcium chloride or silica gel as drying agent. Far more rapid and sufficient drying is, however, obtained with a vacuum desiccator. The desiccant for the removal of water is generally phosphoric anhydride mixed with charcoal; and for organic solvents silica gel or thin slivers of paraffin are used. Almost every solid organic compound can be purified by crystallization. The necessary modifications for crystallization are:

(*i*) If the solubility of the organic compound to be purified is same in cold as in hot solvent, crystallization is carried out by spontaneous evaporation. For this, a concentrated solution is prepared and allowed to evaporate slowly, with the slow evaporation of solvent, the solution becomes more and more concentrated and finally results in the separation of solute as fine crystals.

(*ii*) If the given solute is very much soluble in a solvent 'A' and very sparingly soluble in another solvent 'B'; and 'A' is miscible with 'B', further 'B' has higher boiling point than 'A', their mixture will be very useful for crystallization. This may be illustrated as under: *m*-dinitrobenzene is more soluble in alcohol than water. For crystallization of *m*-dinitrobenzene a concentrated solution of this is prepared in alcohol water is added to this solution slowly until turbidity occurs. The turbid solution is allowed to cool. It would result in the evaporation of alcohol leaving the solution rich in water in which the substance is insoluble. Hence, crystals of *m*-dinitrobenzene would separate out. Pairs of miscible solvents frequently employed for this purpose are:

(1) Alcohol + Water,
(2) Alcohol + Ether,
(3) Petroleum ether + Benzene,
(4) Ether + Acetone,
(5) Benzene + Ligroin, etc.

For crystallization give the following compounds to the students: (*i*) Benzoic acid, (*ii*) Acetanilide, (*iii*) Sugar.

7

Criteria of Purity

When the organic compound has been isolated and the purification has been attempted, the next step is, to check and confirm its purity. A pure organic substance has characteristic physical properties such as definite crystalline form, refrective index, specific gravity, melting point and boiling point. If the compound after purification shows the properties that the pure compound is known to possess, it may be considered pure. The nature and amount of impurities present, however, cause a marked deviation in these characteristic properties. In most laboratory work, the melting point of a solid substance and boiling point of a liquid substance is considered a sufficient indication.

7.1 DETERMINATION OF MELTING POINT OF A SOLID

The accurate determination of melting point of an organic compound plays a very important role, in its identification. The melting point of crystalline solid is the temperature at which the solid begins to change into liquid under a pressure of one atmosphere. For a pure substance the melting range, i.e., the difference between the temperature at which it starts melting and the temperature at which whole of the solid has completely melted, should not exceed more than 0.5°C. If the liquid is cooled, solidification will occur at the same temperature (melting point), and for a pure substance the melting point and freezing point are identical. The freezing point of a substance is defined as the temperature at which the solid and liquid phases of the substance exist together under a pressure of one atmosphere. The apparatus used for the determination of melting point is shown in Fig. 7.1.

Experimental details. The experimental method in most common use is to heat a small amount (neary 1-2 mg) of the substance in a capillary tube attached to a thermometer which is immersed in a suitable liquid bath, and to determine the temperature at which melting occurs.

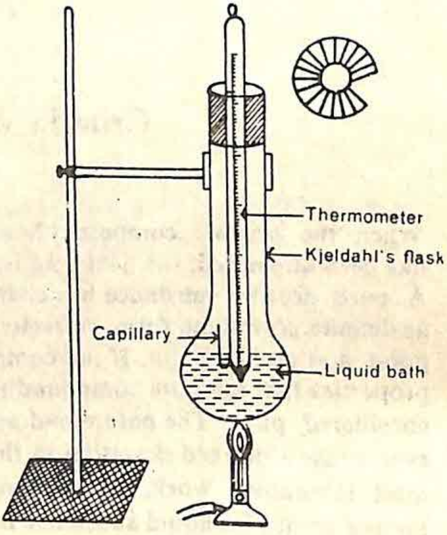


FIG. 7.1. (Determination of melting point).

The pure and dry compound under identification is finely powered on a clean porcelain plate with the help of a clean metal, glass or plastic spatula and then formed into a small mound. A thin capillary of uniform bore and about 5 cm in length is sealed at one end by keeping it in the outer flame of the Bunsen-burner. The open end of the capillary tube is pushed into the finely powdered substance placed on the porcelain plate and then shaken down the tube by tapping the closed end on the tile or working table. The operation is repeated till about 0.5cm long compact filling is obtained. This is a rapid operation when the compound gives a fine dense powder; some compounds, however, even when pure, have a waxy consistency, and are not easily inserted into the capillary tube of the usual width, in such cases a slightly wider capillary (2 mm in diameter) should be used.

The filled capillary tube is then placed along the thermometer with its sealed end near the bulb of thermometer (which has been previously wetted with the bath liquid). The capillary clings to the thermometer due to the surface-tension and viscosity of the liquid. Generally, concentrated, sulphuric acid is used in heating-bath but it is safer to use liquid-paraffin in place of sulphuric acid. The thermometer, with the tube attached, is inserted into the centre of the bath. The thermometer is held in a position as to keep half of the capillary out of the liquid. In case a long necked Kjeldhal flask of 100ml capacity is used as a bath, then thermometer is fitted through a cork, having a shallow vertical groove cut or filed to allow expansion of the contents of the Kjeldhal flask. The flask is then heated with low flame, by holding the burner in hand and rotating the flame over the flask so that the temperature of the bath rises uniformly. The capillary and the rise of mercury in thermometer are noted from time to time. The temperature in thermometer is recorded when the opaque solid in the capillary starts becoming transparent. It is essential for an accurate determination that the temperature of the liquid bath should rise very slowly as the compound is about to melt. After determining the melting point using one tube, the temperature is then allowed to fall about 30°C and second capillary is then substituted for the first, and an accurate determination with the temperature very slowly rising is then made. One should note that a second determination is never made by noting the freezing point, i.e., the temperature at which the molten material solidifies. A freshly filled capillary should be used for each subsequent determination.

7.2 DETERMINATION OF MIXED-MELTING POINT

The presence of impurities as already pointed out causes appreciable deviation in the melting point, the mixed-melting point, therefore, is determined to establish the purity of the substance. The compound under investigation is mixed intimately with a pure sample of same compound in almost equal proportions, and the melting point of the mixed specimen is determined in the usual manner. If the value of the melting point of the mixture is the same as that of pure compound then the compound under investigation is pure. On the other hand, if the melting point of the mixture shows some deviation from the reported actual melting point of the substance, then it is considered as impure. Further, one should keep in mind that some times the deviation in the mixed melting point may be due to the formation of an addition compound on mixing the components. Thus identification by mixed melting point is although a valuable and frequently used process, yet it suffers from some defects and should, therefore, be used with reasonable care, i.e., keeping in mind the possibility of the formation of new compound or optical isomers etc.

Precautions. (*i*) The use of rubber bands for holding the capillary tube should not be done as it blackens the bath liquid which in majority of cases is concentrated sulphuric acid.

(*ii*) Any substance adhering to the outside of the capillary tube must be wiped off so that it will not discolour the bath.

(*iii*) If Kjeldhal flask is used as a bath, then the cork should have a vertical groove so that the thermometer scale is visible and also to allow free expansion of the air in the apparatus.

(*iv*) If possible use medicinal paraffin as a heating liquid because it has a low specific heat, is non-inflammable and non-corrosive.

(*v*) Concentrated sulphuric acid, if used as a heating liquid, should contain a few crystals of potassium nitrate to prevent charring and consequent darkening in colour at high temperature.

(*vi*) Use of sulphuric acid should generally be avoided in elementary classes. If its use is unavoidable due to certain reasons then students should be advised to place a sand-bath on the working table below the acid-bath. This will soak the acid if the bath breaks due to carelessness or irregular heating.

7.3 DETERMINATION OF BOILING POINT OF A LIQUID

The boiling point of organic liquids has the same importance for their indentifications as the melting point of solids. The boiling point of a liquid is defined as the temperature at which the vapour pressure of the liquid is equal to the external pressure exerted at any point upon the liquid surface. This external pressure may be exerted by atmospheric air, by other gases, by vapour and air etc. Thus, by changing the external pressure, the boiling point of the liquid can also be changed. The boiling point at one atmosphere pressure is termed as the *normal boiling point*.

The boiling-point of a pure liquid, which distills without decomposition, is sharp and remains constant until the whole of the liquid has boiled off. Non-volatile impurities do not affect the boiling point. If the impurities are volatile, then the boiling point of the liquid may (1) remain constant, or (2) rise steadily as the liquid boils, or (3) rise in a series of definite steps, according to the nature and quantity of impurities present.

Experimental determination of boiling-point. Unless only minute quantities of the liquid whose boiling point is to be determined, are available, the boiling point is usually determined by simple distillation. A simple distillation apparatus, such as that pictured in Fig. 7.2 is used for this purpose. A distillation flask *A* of suitable size (depending upon the amount of liquid) is fitted to a water-condenser (Liebig's condenser) *B*, the water supply of which is arranged as shown. At the end of the water condenser an adaptor '*C*' is fitted to facilitate the collection of the distillate in the receiver *D*. The thermometer '*E*' of suitable temperature range's fitted into the neck of the distillation flask by means of a well-bored cork, the bulb of the thermometer should be in the centre of the neck of the flask and slightly below of the level of the side tube *S*. The liquid under indentification is then introduced into the flask to have a three-fifths filled capacity. Almost all the liquids super heat to some extent to cause a metastable condition which is interrupted periodically by a sudden violent surge of vapour from the liquid called *bumping*. This may be avoided by the addition of 2 or 3 small fragment of unglazed porcelain or pumice stones to the distilling flask. The small pores of the boiling stones provide a site for the formation of bubble nuclei and thereby induce even-boiling. After adding boiling chips, the thermometer is placed in position and the flask is then heated-either on a water bath if the liquid has a low boiling-point, or else on a sand-bath, or directly on a wire gauze. Distillation should always be conducted slowly but steadily so that the thermometer bulb at all times bears a drop of condensate. This favours the maintenance of equilibrium between liquid and vapour at the bulb.

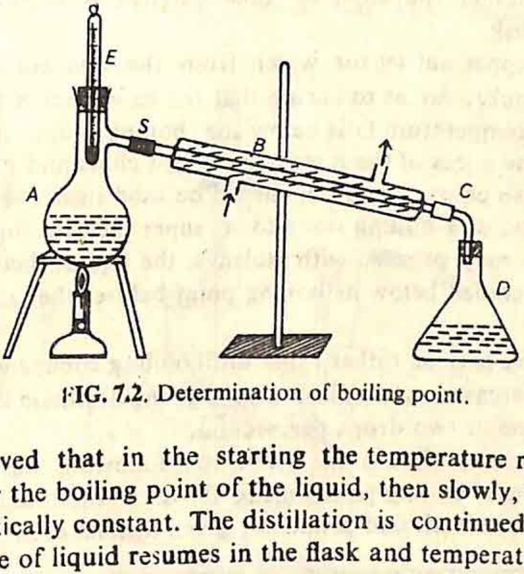


FIG. 7.2. Determination of boiling point.

It is observed that in the starting the temperature rises rapidly until it is near the boiling point of the liquid, then slowly, and finally becomes practically constant. The distillation is continued until only a small volume of liquid resumes in the flask and temperature is noted at regular intervals. If the liquid is pure, most of it would distill off at constant temperature (within 0.5°C), this constant temperature is the boiling-point of the liquid. Superheating may cause a slight increase in the temperature towards the end of the distillation, a necessary correction, therefore, may be applied to obtain the correct boiling point.

Precautions. (*i*) The fragments of unglazed porcelain should always be added whenever a liquid is distilled.

(*ii*) Low-boiling (boiling-point below 80°C) inflammable liquids are usually distilled from a water-bath.

(*iii*) For liquids of higher boiling-point (more than 80°C) a sand bath or direct heating on a gauge is necessary.

(*iv*) A water-condenser should be used for any liquid having boiling point below 140°C. Above this temperature, an air-condenser (a straight glass tube without any jacket) should be used.

(*v*) All corks should fit tightly, in the apparatus may be used for inflammable liquids.

(*vi*) The size of the distillation flask should not be too large as it will favour super heating and, sometimes, decomposition of the liquid also.

(*vii*) The liquid should be poured into the distilling flask, preferably through a funnel the stem of which extends below the side arm of distillation flask.

(*viii*) The upper out-let for water from the condenser should be above the jacket so as to ensure that the condenser is full of water.

(*ix*) If the temperature falls below the boiling point at any time, liquid fills the pores of the porous-porcelain chips and it is no longer effective. Fresh chips, therefore, should be used then.

(*x*) Addition of a boiling stone to a super heated liquid initiates boiling that may proceed with violence, the liquid, therefore, should definitely be cooled below its boiling point before the addition of a fresh chip.

(*xi*) Heating may be rather rapid until boiling commences, the flame then the decreased and adjusted so that the destillate is collected at the rate of one or two drops per second.

Note. Students should be given the following liquids, for the determination of boiling points using above method and should be instructed to use bath and condenser given against each.

Liquid	*Boiling point°C*	*Bath*	*Condenser*
1. Acetone	56	Water-bath	Water-condenser
2. Benzene	81	Sand-bath	Water-condenser
3. Aniline	184	Sand-bath	Air-condenser
4. Nitrobenzene	210	Sand-bath	Air-condenser

7.4 SIWOLOWOFF'S METHOD FOR THE DETERMINATION OF THE BOILING-POINT

This method is used when only minute quantities of liquid are available. A simple apparatus, such as pictured in Fig. 7.3 is used for this purpose. A small quantity (0.25-0.5 ml) of the liquid, (under identification is taken in a thin walled ignition tube which is attached to the thermometer by a rubber-band and the thermometer is immersed in a bath containing sulphuric acid. A capillary about 5 cm long and sealed at about 1 cm away from one end is put into the ignition tube containing liquid under identification. The acid bath is then heated gradually and with stirring. The air bubbles from the end of the capillary tube start escaping at a slow rate, but when the boiling point of the liquid is attained, a rapid and continuous escape of air bubbles will be observed. The reading of the thermometer when a rapid and continuous stream of air bubbles first emerges from the capillary tube is taken and heating discontinued. The thermometer is

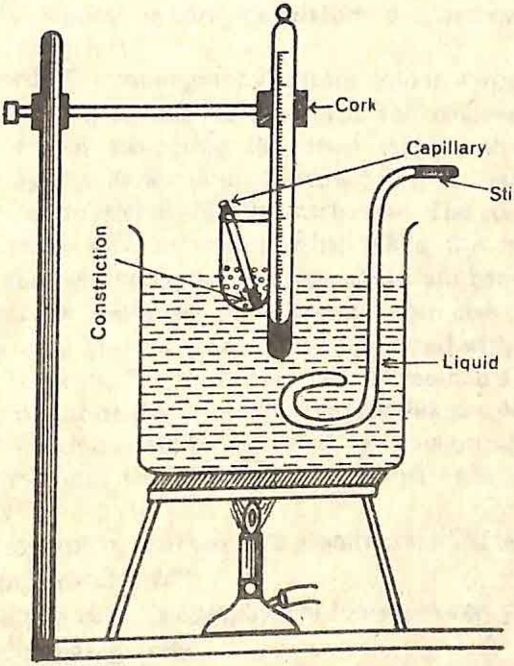


FIG. 7.3. Siwolowoff's method of determining boiling point of a liquid.

again read when the last bubble makes its appearance and exhibits a tendency to such back. This temperature is the point at which the vapour pressure of the liquid is equal to that of the atmosphere. The mean of the two readings is the accurate boiling point of the liquid. As an additional check, the experiment is repeated, i.e., the bath is allowed to cool a few degrees and both the readings are taken with a fresh amount of liquid. If the boiling point obtained is the same for the second time also, the liquid may be considered as pure.

8

Paper Chromatography and Thin Layer Chromatography

Introduction

Organic chemical reactions usually yield mixtures of products which must be separated and analysed if the reactions are to be understood and made useful. One of the techniques used for this purpose is chromatography. It is the name given to a family of methods for separating complex mixtures and determining the amount of their constituents.

The word 'Chromatography' means colour writing and was introduced by Mikhail Tswett. He separated the coloured substances in green leaves, by extracting the dried leaves with petroleum othei, then pouring the dark-coloured extract into a vertical glass tube packed with powdered calcium carbonate. The coloured substances were separated with petroleum ether when the two chlorophylls, carotion and xanthophylls got separated into bands. Of course the technique is not restricted to coloured substances only, colourless substances can also be separated and detected with chemical colour producing reagents. The advantages of this method are its ability to:

(*i*) separate substances from the complex mixture of closely related substances which can not be separated by ordinary chemical methods;

(*ii*) separate mixtures of very small quantities or at very low concentrations.

Chromatographic methods are usually classified according to their most obvious features as:

(*a*) Gas-liquid chromatography, (*b*) Ion-exchange chromatography, (*c*) Paper chromatography.

We shall only discuss the technique of paper chromatography. The essentials of chromatography are: a fixed or stationary phase—usually a finely divided granular solid; a moving phase—which can be a gas or a liquid; and the substrates or solutes that are to be separated.

Paper and thin layer chromatography do not use column, the fixed phase in one case is a sheet of filter paper and in the other case a layer of finely divided adsorbent spread on a plate of glass or plastic. Both paper and thin-layer chromatography are used extensively in biochemistry for the analysis of complex mixture like mixtures of amino acids or sugars and in geochemical prospecting.

8.1 PAPER CHROMATOGRAPHY

In paper chromatography the moving liquid flows between the fibres of cellulose, but these are not the true stationary phase ; the ture stationary phase is a very thin film of liquid, usually water, adhering to the surface of the fibres. The fibres are filled with water and the developing solvent cannot flow. However, if the fibres are really dry the substrates will not move. Thus paper chromatography will not work in dry climates unless the paper is exposed to air of high humidity, before being placed in the developing solvent. Paper chromatography is a kind of partition chroma-

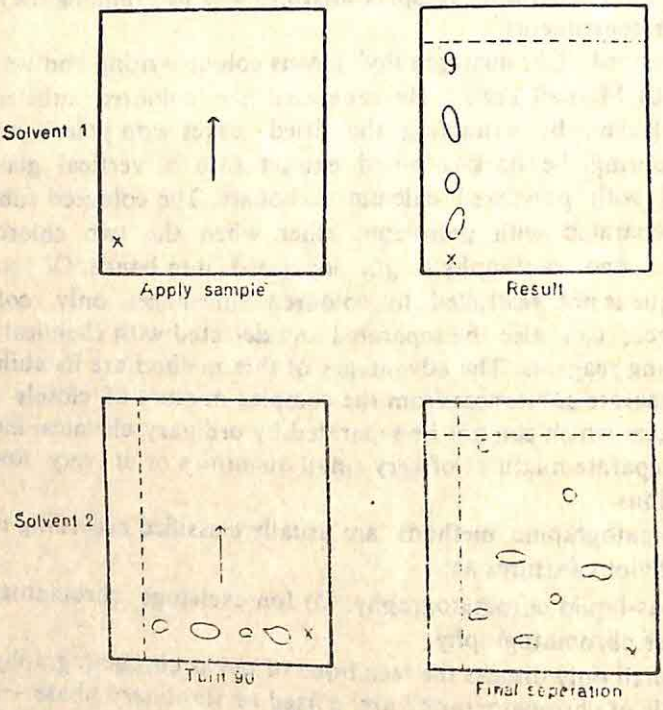


FIG. 8.1

tography in which the substrates are distributed between two liquids, the stationary liquid that is held on the fibres of the paper, and the moving liquid or developing solvent. Normally one uses whatman No. 1 grade of filter paper which is cut into a rectangular strip 2 cm wide and 15cm long. For running several samples side by side it is convenient to use slotted paper as shown in Fig. 8.1.

The slots can be cut out of ordinary rectangular sheets with a razor blade. Samples for chromatography are placed about 2 centimeters from one end of the paper; in the form of spots or narrow horizontal lines. Generally they are applied as solutions and are dried. This paper is developed by allowing the solvent, to rise up the length of the paper. Rectangles of paper may be rolled into a cylinder, fixed with a paper clip and is made to stand upright in a cylindrical jar, which is then enclosed with a watch glass.

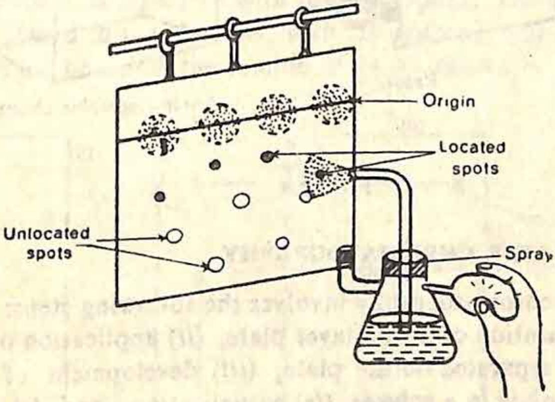


FIG. 8.2 (a)

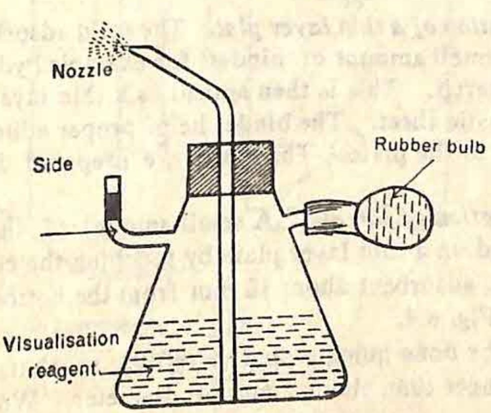


FIG. 8.2 (b)

In the arrangements shown in Fig. 8.2, when the solvent is moving up ward through the paper; these arrangements are called ascending paper chromatography. There is another arrangement called descending paper chromatography in which the solvent is contained in a small trough at the top of the developing tank. Fig. 8.3 (*a*) and (*b*).

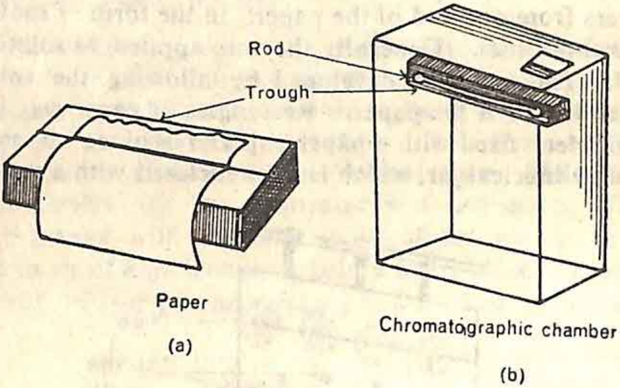


FIG. 8.3

8.2 THIN LAYER CHROMATOGRAPHY

Thin layer chromatography involves the following steps:

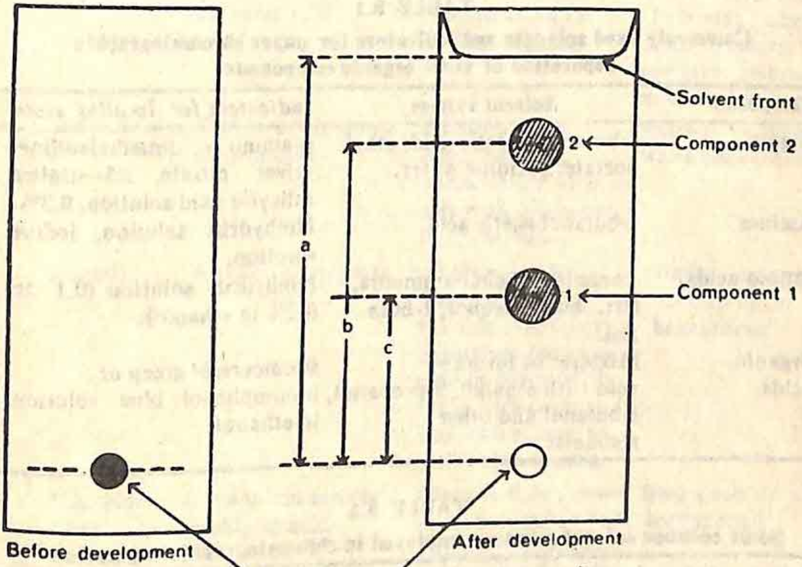
(*i*) Preparation of a thin layer plate, (*ii*) application of the materials to be separated on the plate, (*iii*) development of the chromatogram plate in a solvent, (*iv*) visualisation, and (*v*) calculation of R_f values.

(*i*) *Preparation of a thin layer plate*. The solid adsorbent is usually mixed with a small amount of 'binder' for example hydrated calcium sulphate or starch. This is then spread as a thin layer on a glass plate or a plastic sheet. The binder helps proper adherence of the adsorbent on to the plate. The plates are prepared in the laboratory.

(*ii*) *Application of sample*. A small amount of the solution is then deposited on a thin layer plate by touching the capillary to the surface of the adsorbent about 10 mm from the bottom of the plate as shown in Fig. 8.4.

This must be done quickly and carefully so that the resulting spot is no longer than about 2 mm in diameter. When a solution of concentration, it is necessary to apply more solution on the spot until sufficient sample is accumulated. The spot should be allowed to dry between additions. The position of the spot is marked with pencil, so that R_f values may be calculated after separation. When more than one spot of the sample is being analysed on the same plate, the spot must be deposited symmetrically at least 5 mm apart. The spot should be dry, before the plate is developed.

(*iii*) *Development of the thin layer plates.* The plate is then placed in development chamber which is prepared by covering a beaker tightly with aluminium foil. A filter paper touching the bottom of the chamber is placed against the inside wall to promote rapid equilibrium between liquid and vapour. The development solvent is now added in an amount sufficient enough to saturate the filter paper and leave a layer of 5—6 mm in depth at the bottom. The chamber is then allowed to stand for few minutes until the atmosphere within, is saturated with solvent vapour. The thin layer plate is now placed in the chamber, with its spotted end down the solvent level must be below the sample spots as shown in Fig. 8.4.



$$R_f\ (\text{component 1}) = \frac{c\ \text{cm}}{a\ \text{cm}}$$

$$R_f\ (\text{component 2}) = \frac{b\ \text{cm}}{a\ \text{cm}}$$

FIG. 8.4 Chromatographic Chamber.

Cover the chamber immediately and leave it undisturbed until the solvent has moved 3/4 of the way up the plate. The plate is now removed and mark the position of the solvent front with a pencil.

(*iv*) *Visualization.* The spots due to the materials present after separation, on the chromatogram, can be detected by simple visual examination. Spots of some colourless compounds which are invisible to the eye but which fluoresce can be detected by irradiation of the plate with ultraviolet light. Sometimes a suitable reagent for visualisation of the spots can be sprayed on to the plate.

(*v*) *Calculation of R_f values.* The R_f value is characteristic of a compound under specified conditions. The R_f value is defiend as,

$$R_f = \frac{\text{distance travelled by sample in cm}}{\text{distance travelled by solvent in cm}}$$

Tentative identification can however be made by comparing R_f values of unknown samples and known compounds using several different solvent systems. Sometimes different compounds may have identical R_f values in one solvent but they will have different values in another solvent.

TABLE 8.1

Commonly used solvents and indicators for paper chromatographic separation of some organic compounds

Compound	*Solvent system*	*Indicators for locating spots*
Sugars	1-butanol; acetic acid; ethyl acetate; pyridine water.	p-amino dimethylaniline; silver nitrate, 3:5—dinitro salicylic acid solution, 0.3%.
Amines	1-butanol-acetic acid.	Ninhydrin solution, iodine solution.
Amino acids	Phenols: phenol-ammonia, tert. butyl alcohol, 1-butanol.	Ninhydrin solution (0.1 to 0.2% in ethanol).
Organic acids	Mixtures of formic—acid with ethanol, 2-propanol, 1-butanol and other alcohols.	Bromocresol green or bromophenol blue solution in ethanol.

TABLE 8.2

Some common solvent mixures employed in chromatographic separation

Solvent mixture 1.	Ethanol (7 volumes) + Distilled water (3 volumes).
Solvent mixture 2.	Butanol (6 volumes) + Glacial acetic acid (1 volume).
Solvent mixture 3.	Acetone (17 volumes) + Distilled water (1 volume) + concentrated hydrochloric acid (2 volumes).
Solvent mixture 4.	n-Butanol (3 volumes) + Ethanol (1 volume) + 2M aqueous ammonia solution (1 volume).

TABLE 9.3

Specific Spray Reagents for Functional Groups.

Compound class	*Reagent*	*Procedure*	*Results*
Acids	Bromocresol green	Dissolve 0.4g in 100ml ethanol, add 0.IN NaOH until colour just appears.	Yellow spot.
	2,6-dichlorophenol indophenol (sodium salt)	Dissolve 0.1g in 100 ml ethanol.	Red spots on the blue background.
Alcohols	Ceric ammonium nitrate	Dissolve 6g in 100ml 4N HNO_3.	Brown spots on yellow background.
	vanadium oxinate	Dissolve 0.1g in 100ml alcohol free chloroform.	Red spots on green background.
Amines	Cobalt thiocyanate	Dissolve 3g ammonium thiocyanate and 1g cobalt chloride in 20ml water.	Primary, secondary and tertiary aliphatic amines give blue spots on white background.
	salicylic acid	Dissolve 1g in 100ml toluene.	Primary, abphatic and aromatic amines give yellow spot on white background.
Antioxidants	Dichloroquinone-4-chloroimine	Dissolve 1g in 100ml ethanol, respray after 15 minutes with 2% borax in 4% ethanol.	Various colours on white background.
Phenols	4-amino antipyrene	(a) Dissolve 3g 100ml ethanol. (b) Dissolve 8g of potassium ferricyanide in 100ml H_2O; spray with (a) then (b) and then expose to ammonia vapours.	Red, orange or pink spots on pale background.
Phosphate esters	Ammonium molybd. perchloric acid	Dissolve 0.5g ammonium molybd in 5ml water and 1ml conc. HCl; add 2.5ml perchloric acid and cool, dilute to 50ml with acetone and allow to stand for 24 hrs; after spraying expose for two minutes	Blue spots on white background.

Compound class	*Reagent*	*Procedure*	*Results*
		to an IR lamp, then 7 minutes to longwave-UV light.	
Polynuclear aromatic hydrocarbons	Formaldehyde-sulphuric acid	Dissolve 2ml 37% formaldehyde solution in 100ml conc. H_2SO_4	Various colours on white background.

Exercise 8.1. *To separate the components of chlorophyll by ascending paper chromatography.*

Principle. The fresh green parts of plants contain two green pigments, chlorophyll (*a*) ($C_{55}H_{72}O_5N_4Mg$), chlorophyll (*b*) ($C_{55}H_{70}O_6N_4Mg$) and xanthophyll in a ratio of 12:2 :1: .002.

All the four components have different adsorption power or an affinity for a particular adsorbent. When the mixture is chromatographed on a paper strip using petroleum-ether and acetone (9:1) mixture as solvent. The weakly adsorbed ones move rapidly, along with solvent front and have a high R_f value, whereas strongly adsorbed ones move slowly as these possess low R_f values. All the pigments have a colour of their own, so no reagent is needed to form coloured derivatives of them.

Method. Take small amount of grass, cut it into small pieces. Triturate it with almost an equal amount of sand and 5ml of acetone. Take out this solution in a test tube. Take a chromatographic tube, wash it with chromic acid and dry. Pour into it a mixture of petroleum-ether and acetone (9:1). Cut a piece of Whatman No. 1 paper (15cm × 1.5cm) and put a spot of the (acetone+chlorophyll) solution on the paper as explained earlier. Dip the paper into the solution. The chromatogram is developed after 45 minutes.

Calculate the R_f values of the constituents as explained earlier. Record their respective R_f values and also attach the chromatogram.

Exercise 8.2. *To separate a mixture of dyes using ethanol-water.*

Principle. A mixture of dyes can be separated using ascending paper chromatography when a set of several spots are obtained on a chromatogram. The number of spots will be equal to the number of dyes in the mixture. The R_f of each dye can be obtained by measuring the total distance travelled by the solvent front and the distance travelled by each dye from its visualised spot.

Materials required. Solution of the given mixture of dyes; a mixture of 1:1 ethanol and water; Whatman filter paper.

Procedure. Cut a strip of Whatman filter paper 12cm in length. Draw the origin line about 1cm from one end of the strip and apply the given mixture in a spot about 5mm in diameter at the centre of the origin line. Dry the spot and suspend the paper vertically in a chromatography tank containing the solvent (ethanol-water, 1:1). Cover the lid of the tank for about 45 minutes. Make sure that the solvent has ascended about 9cm on the paper. Remove the paper from the tank mark the position of the solvent-front on it. Dry the paper in the air. Count the number of spots that will give the number of dyes in the mixture and calculate the R_f value for each dye.

Result: The given mixture was found to contain the dyes............

Exercise 8.3. *To sparate a mixture of sugars by paper chromatography.*

Materials required. Chromatographic tank, ethyl acetate glacial acetic acid—water as the solvent system;p-anisidine hydrochloride (1.5% solution); mixture of sugars (glucose, fructose and xylose)

Procedure. Cut a strip of Whatman filter paper No. 1 of size 12cm × 1.5cm. Draw the origin line obout 1cm from one end of the strip. Apply the given mixture in a spot about 5mm in diameter at the centre of the origin line. Dry the spot and suspend the paper in a vertical position in the chromatographic tank. The end origin line should dip in the solvent. The solvent is a mixture of ethyl acetate (54 volumes), glacial acetic acid (12 volumes) and water (12 volumes). Let the paper stand in the tank for about half an hour.

Remove the paper from the tank and dry it. Spray the paper with 1.5% p-anisidine hydrochloride which acts as a visualising agent. Dry the paper for five minutes in an oven between 80°C and 100°C. The separated sugars will appear as yellowish-brown spots. Determine their respective R_f values.

9

Detection of Extra-elements in Organic Compounds

A knowledge of the elementary constituents is essential for the characterisation of any unknown organic compound. Before the usual qualitative tests can be applied, the elements must be converted from the covalent form, in which they usually occur in organic compounds into ions or simple compounds for which routine tests are available. In general, all organic compounds are expected to contain carbon and hydrogen, therefore, it is not necessary to test for the presence of these elements. The elements which commonly occur in organic compounds along with carbon, hydrogen and oxygen, and with which we are primarily concerned, are: nitrogen, sulphur and the halogens (Cl, Br, I).

The method for the detection of nitrogen, sulphur and halogens depends upon the fact that fusion with sodium, of an organic compound containing these elements, converts them to easily identifiable ions

$$\mathrm{C, H, O, N, S, X} \xrightarrow[\text{with Sodium}]{\text{Fusion}} \begin{cases} \mathrm{NaCN} \\ \mathrm{NaCNS} \\ \mathrm{Na_2S} \\ \mathrm{NaX} \end{cases}$$

(all are water soluble)

Based upon the above principle, J.L. Lassaigne introduced a very important and most widely used method for the detection of these elements in 1843, which, after his name, is known as Lassaigne's Test.

9.1. THE LASSAIGNE'S TEST

Preparation of Lassaigne's filtrate (sodium extract); caution: Wear safety-glasses before you proceed for the preparation of sodium extract. Introduce a small piece (about half the size of a pea) of freshly cut, clean and dry sodium, into an ignition-tube, held in a vertical position, with a pair of tongs. Heat the lower part of the tube in a Bunsen-flame gently, till sodium melts to form a shining globule. Remove the ignition tube from the flame and then insert a small amount (about 0.1g for solids and 2-3 drops for liquids) of the organic substance under indentification. Allow the brisk reaction, if any, to subside and heat the ignition tube on the flame for a few seconds. If the reaction becomes vigorous, it should be removed from the flame immediately. Again heat it first over low flame and then strongly till it becomes red hot or starts melting. The fusion tube should not point toward any one. Plunge the hot tube into a porcelain-dish containing 10ml of distilled water and immediately cover the dish with a wire-gauge, to prevent any unreacted sodium or of broken glass pieces from flying off the dish. Crush any unshattered portion of ignition tube with the help of a glass rod and boil the contents of the dish for about five minutes and filter. The filtrate should be clear like water, if it is coloured than it indicates incomplete fusion and the entire process should be repeated. The filtrate is known as Lassaigne's filtrate or sodium-extract. Retain the filtrate as a stock solution for the subsequent tests.

9.2. TEST FOR NITROGEN

To 3ml of the filtrate add about 0.2g of ferrous sulphate crystals or 5 drops of a fresh 5 per cent solution of ferrous sulphate and 5 drops of a 10 per cent solution of potassium fluoride. A dark greenish-grey precipitate of ferrous hydroxide should occur (if the organic compound contains sulphur a black precipitate may be produced at this stage), if the mixture remains clear, add a few drops of sodium hydroxide solution. Boil the resulting mixture gently for one or two minutes to facilitate arial oxidation of ferrous ions into feric ions. Cool and add sufficient dilute, i.e., 25 per cent sulphuric acid to dissolve the insoluble iron oxides and make the solution clear. Appearance of a brilliant blue solution or suspension of Prussian blue confirms the presence of nitrogen in the original organic compound. Sometimes, a greenish-blue colour is also obtained, which suggests that nitrogen is present but the fusion was incomplete.

Chemistry of the test. Nitrogen appears in the fusion product as cyanide ion,

$$\mathrm{Na}+\underbrace{\mathrm{C}+\mathrm{N}}_{\text{(from organic compound)}} \xrightarrow{\text{Fusion}} \underset{\text{(water soluble)}}{\mathrm{NaCN}}$$

The latter is extracted with water. On the addition of ferrous sulphate and then boiling the alkaline mixture in order to convert the cyanide into ferrocyanide:

$$6NaCN + Fe(OH)_2 \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$$

Ferrocyanide, then, reacts with Fe^{3+} ions produced during arial oxidation of $FeSO_4$, to give a Prussian blue colour of ferri-ferrocyanide:

$$3Na_4[Fe(CN)_6] + 4Fe^{3+} \dashrightarrow \underset{\text{Ferri-ferrocyanide (Prussian blue)}}{Fe_4[Fe(CN)_6]_3} + 12Na^+$$

Note. The use of hydrochloric acid for acidifying the alkaline solution should be avoided as the yellow colour due to ferric chloride formed, causes the prussian blue to appear greenish. For the same reason, ferric chloride should not be added.

9.3. TEST FOR SULPHUR

(a) Sodium nitroprusside test. To 2ml of the sodium extract, add a few drops of a freshly prepared dilute solution of sodium nitroprusside, $Na_2[Fe(CN)_5NO]2H_2O$. A brilliant purple coloration (resembling permanganate) confirms sulphur; the coloration slowly fades on standing.

$$\underset{\text{(From sod-extract)}}{Na_2S} + Na_2[Fe(CN)_5NO] \dashrightarrow \underset{\text{(Purple-colour)}}{Na_4[Fe(CN)_5NOS]}$$

Note. Sodium nitroprusside is unstable in aqueous solution and therefore, the solution should be freshly prepared on each occasion.

(b) Lead-acetate test. Acidify 2ml of the sodium extract with dilute acetic acid and add 5 drops of lead acetate solution. A black precipitate of lead sulphide indicates the presence of sulphur.

$$Na_2S + Pb(CH_3COO)_2 \dashrightarrow \underset{\text{(Black ppt.)}}{PbS\downarrow} + 2CH_3COONa$$

Combined test for nitrogen and sulphur. If the given organic compound contains nitrogen in addition to sulphur, then sodium thiocyanate, NaCNS, is produced during ignition. Sodium thiocyanate forms a blood-red coloration with ferric-chloride solution.

$$Na + S + N + C \xrightarrow{\text{ingition}} \underset{\text{(water soluble)}}{NaCNS}$$

$$3NaCNS + FeCl_3 \dashrightarrow \underset{\substack{\text{(Ferric-sulphocyanide)}\\ \text{(Blood-red)}}}{Fe(CNS)_3} + 3NaCl$$

9.4. TEST FOR HALOGENS

(a) Nitrogen and sulphur being absent: **In this case halogen has been converted into the corresponding sodium halide during the sodium fusion. Therefore, acidify 3ml of the filtrate with dilute nitric acid** and add a few drops of silver nitrate solution. A white or yellow precipitate indicates halogen.

(*i*) A curdy white precipitate, soluble in NH_4OH indicates chlorine in the organic compound.

(*ii*) A light yellow precipitate sparingly soluble in NH_4OH indicates bromine.

(*iii*) A pale yellow precipitate insoluble in NH_4OH indicates the presence of iodine.

Chemistry of the test.

$$NaX\ (X=Cl,\ Br,\ I)+AgNO_3 \xrightarrow{\text{dil. }HNO_3} AgX\downarrow+NaNO_3$$

when $X=Cl$; $AgCl=$White ppt.

$$\underset{\text{(excess)}}{AgCl+2NH_4OH} \longrightarrow \underset{\substack{\text{Silver aminochloride}\\\text{(Soluble)}}}{[Ag\ (NH_3)_2]\ Cl} +2H_2O$$

when $X=Br$; $AgBr=$Light yellow ppt.

$$AgBr+2NH_4OH \longrightarrow \underset{\text{(Sparingly soluble)}}{[Ag(NH_3)_2]\ Br} +2H_2O$$

when $X=I$; $Ag\ I=$Yellow ppt.

$$AgI+NH_4OH \longrightarrow \text{No reaction.}$$

(b) **Interference due to nitrogen and sulphur.** When nitrogen or sulphur, or both, are present they interfere in the detection of halogens. The addition of $AgNO_3$ to acidified sodium extract precipitates silver cyanide or silver sulphide

$$NaCN+AgNO_3 \xrightarrow{\text{dil }HNO_3} AgCN\downarrow+NaNO_3$$

$$Na_2S+2AgNO_3 \xrightarrow{\text{dil }HNO_3} Ag_2S\downarrow+2NaNO_3$$

Hence, before we proceed for the detection of halogens, nitrogen and sulphur should be eliminated from the sodium extract. This is done by boiling sodium extract with a few drops of concentrated HNO_3 for 3-4 minutes which expells all H_2S and HCN.

$$NaCN+HNO_3 \xrightarrow{\text{boiling}} HCN\uparrow+NaNO_3$$

$$Na_2S+2HNO_3 \xrightarrow{\text{boiling}} H_2S\uparrow+2NaNO_3$$

The solution obtained after the expulsion of N, and S as HCN and H_2S is then tested for halogens as described earlier.

Test for bromine and iodine. (When either of the two is present)

Acidify 2ml of the sodium extract with dil HNO_3.

Add 1-2ml of acidified $KMnO_4$ or chlorine water in excess and 2ml of CCl_4, $CHCl_3$ or CS_2. Shake the contents of the test tube and allow it to stand for 2-3 minutes.

(*a*) A violet colour in lower (organic) layer confirms iodine.

(*b*) A brownish colour in lower (organic) layer indicates bromine.

Chemistry of the test. $NaBr + HNO_3 \longrightarrow NaNO_3 + HBr$

$$2HBr \xrightarrow[\substack{\text{by}\\ \text{acidified } KMnO_4\\ \text{or}\\ \text{Chlorine water}}]{\text{oxidation}} Br_2 + H_2O$$

Bromine is absorbed in the organic solvent, i.e., CCl_4 or $CHCl_3$ or CS_2. The brown colour is due to absorbed bromine in organic solvent which being heavier and insoluble in water forms a lower layer.

$$NaI + HNO_3 \longrightarrow HI + NaNO_3$$

$$2HI \xrightarrow{\text{Oxidn.}} \underset{\substack{\text{(absorbed inorganic solvent,}\\ \text{imparts violet colour)}}}{I_2 + H_2O}$$

Test for bromine in the presence of iodine. The above test is modified as follows: The chloroform test is performed first as described above, when the layer of chloroform turns violet due to iodine. Add excess of chlorine water to this and shake vigorously when the violet colour would disappear due to the oxidation of iodine to iodate. On further shaking if the chloroform layer becomes brown, orange or yellow, bromine is also present but if the chloroform layer remains colourless then bromine is absent.

$$\underset{\text{(from chloroform layer)}}{I_2 + 5Cl_2 + 6H_2O} \longrightarrow \underset{\substack{\text{iodic acid}\\ \text{(colourless)}}}{2\,HIO_3} + 10HCl$$

$$2NaBr + Cl_2 \longrightarrow \underset{\text{(brown or orange)}}{Br_2} + 2NaCl$$

Test for chlorine in the presence of iodine and bromine. To 2ml of sodium-extract in a test tube add 2ml of conc. HNO_3. Boil the solution till the evolution of violet or brown coloured vapours continues, cool and add one ml $AgNO_3$ solution, curdy white precipitate highly soluble in NH_4OH confirms the presence of chlorine.

9.5 THE MIDDLETON'S METHOD FOR DETECTING NITROGEN, SULPHUR AND HALOGENS IN ORGANIC COMPOUNDS

The advantage of this method over Lassaigne's method, is, that the use of metallic sodium, which is toxic in nature and is attacked by moisture very easily, is avoided. It has the disadvantage that the reagents are not so readily obtained pure. Further, the method is more time consuming.

The method suggested by Middleton, in the year 1965 involves the heating of the given organic compound with a mixture of pure sodium carbonate and pure zinc powder, when nitrogen and halogens are split off as sodium cyanide and halides respectively, and sulphur as zinc sulphide. The sodium cyanide and halides, being water soluble, are extracted with water and detected as in Lassaigne's method, zinc sulphide in the residue is decomposed with acid to liberate H_2S which is tested with lead acetate paper. Under these circumstances compounds having nitrogen and sulphur both do not give thiocyanates, a further minor advantage over Lassaigne's method.

Preparation of the reagent. A mixture of 25g of pure, anhydrous sodium carbonate (analar grade) and 50g of the pure zinc dust is grinded in a dry mortar and the reagent is preserved in air-tight bottles until required.

Caution: Zinc dust of good quality is free from nitrogen but is usually contaminated with negligible quantities of sulphur and halogens. It is, therefore, necessary to conduct a blank test (without adding the compound under test) for sulphur and halogens with every batch of the test with the given organic compound.

The fusion. (*i*) *For solid compounds.* Take about 0.2g of the finely powdered solid in a clean and dry hard-glass tube, add sufficient amount of the reagent shake thoroughly to make an intimate mixture of 1cm column. Now add more reagent (without mixing with the material already in the tube) until a total height of about 3-4cm is obtained.

(*ii*) *For liquid compounds.* Add the reagent to the hard-glass tube to a height of about 1cm, 2-3 drops of the liquid under test and allow it to soak well into the reagent. Now add more reagent, without mixing, until a total height of about 4 cm is obtained.

Proceed as follows for both solid and liquid compounds. Hold the test tube in a horizontal position and heat the mixture gently at the open end. Increase the size of the flame gradually until the mixture becomes red hot at the end. Continue the heating slowly, towards the closed end until the whole mixture becomes red hot. In case, the mixture tends to be pushed out of the tube by the evolution of gas during the heating process, heating should be stopped momentarily and the test tube should be rotated in the same position to redistribute the contents. Finally heat the tube strongly for a short time in a vertical position. When the end of the tube becomes red hot, plunge the tube vertically in a china-dish containing 20ml distilled water; boil the contents of the dish and allow to cool. Decant the supernatant liquid by filteration. Retain the residue in the basin for the sulphur test and perform the test for nitrogen and halogens with the filterate as given under Lassaigne's test.

10

Systematic Analysis of Simple Monofunctional Organic Compounds

Organic compound after it is isolated from a natural product or synthesised, is subjected to the process of purification. After ascertaining purity, the next step is, to establish its identity. It must be emphasized here, that unlike systematic inorganic analysis, organic analysis is not so systematised. The problem of characterisation can, however, be made enormously simple by applying the knowledge of organic chemistry, to understand the significance of any observations which may throw light on the analysis. In any scheme of systematic identification the organic compound, has to be subjected to detailed physical and chemical analysis followed by careful interpretation of the data so obtained for establishing its identity. The main steps involved in the systematic investigation of organic compounds include the following steps:

10.1 (*A*) PRELIMINARY INVESTIGATIONS

(*a*) **Physical properties.** The following physical properties are of great use to establish the identity of an unknown organic compounds.

(*i*) *Physical state.* Whether the compound is a solid or liquid, and if solid whether it is crystalline or amorphous. If it is liquid, then its viscosity should be judged. This observation divides all the organic compounds into two classes, i.e., solids and liquids. For a solid, the melting point is of great importance and for a liquid the boiling point is determined. These characteristics are measured as explained in Chapter 7.

(*ii*) *Colour.* The colour of an organic compound is mostly due to the presence of groups with multiple linkages, i.e., chromophoric groups. This suggests that if a compound is colourless or white, then the absence of chromophoric groups is certain. Depending upon the colour some guess can easily be made about the class of compounds. Thus, quinones, nitro compounds, iodoform etc. are yellow in colour, alizarin, phenanthroquinone and o-nitroaniline are orange coloured; 1, 2-napthoquinone is red. Sometimes the colour of the compounds can be misleading also. To illustrate this-phenols, aromatic amines, chloral hydrate, napthalene etc., are generally colourless or light coloured substances but on exposure to light, air or moisture they impart very dark coloures.

(*iii*) *Odour*. Some organic compounds possess characteristic odour, though, there is no distinct relationship between the odour of organic compounds and their chemical constitution. Some organic compounds with their characteristic smell have been listed below:

Pleasant odour. Esters, ethers, acetate, chloroform.

Odour of bitter almonds. Nitrobenzene, benzaldehyde, benzonitrile.

Pungent odour. Acetic acid, acetyl chloride, acetic anhydride, benzoyl chloride, benzyl chloride, benzoquinone, formic acid and pyridine.

Cucumber like odour. Chloral hydrate.

Odour of moth balls. Naphthalene.

Phenolic odour. Phenols and derivatives of salicylic acid.

Mouse-like odour. Acetamide and acetonitrile.

Offensive odour. Isocyanides.

(*B*) SOLUBILITY

The study of the solubility of an unknown compound in some solvents, given below, provides valuable information as to the presence or absence of certain classes of organic compounds. The solubility test should be applied intelligently. For this, place 0.1g of unknown solid comound (if liquid 0.2ml) in a small test tube and add, in portions, with shaking, 3ml of water. If the compound dissolves then repeat the test with ether as the solvent.

If the compound proves to be insoluble in water, test its solubility in 5 per cent sodium hydroxide, if it dissolves in sodium hydroxide test its solubility in 5 per cent sodium bicarbonate solution.

The solubility of the compound, which remains insoluble in sodium hydroxide solution, is further seen in 5 per cent hydrochloric acid. An organic compound which remains insoluble in water, sodium hydroxide, and hydrochloric acid and contains no nitrogen, its solubility is tested in conc. sulphuric acid. The following Chart (Table 10.1) gives the solubility classes of various organic compounds:

TABLE 10.1
Solubility Chart of Organic Compounds

Water soluble		*Water insoluble*				
Ether-Soluble	Ether-Insoluble	Soluble in 5% NaOH Soln.		Insoluble in 5% NaOH Soln.		
Aliphatic alcohols, aldehydes, ketones, amines, carboxylic-acids, amides, esters, lower cyanides, a few anhydrides.	Glycols, aminesalts, polybasic acids, salts of carboxylic-acids, polyhydroxy compounds some amino acids, sugars, some amides, some amines.	Soluble in 5% $NaHCO_3$ Soln.	Insoluble in 5% $NaHCO_3$ Soln.	Insoluble in 5% HCl		
		Carboxylic acids, Nitrophonols.	Some imides, phenols, a few nitro compounds, a few enols, and a few oximes.	Contain Nitrogen	Contain no Nitrogen	
				Amides, Cyanides, nitro compounds, azo compounds hydrazo-compounds.	Soluble in cold Conc. H_2SO_4	Insoluble in cold Conc. H_2SO_4
					Alcohols, aldehydes ketones esters of relatively high molecular weight, quinones, ethers, acetals, lactones, anhydrides and unsaturated hydrocarbons.	Aliphatic and aromatic halides, hydrocarbons.

(*C*) IDENTIFICATION OF THE NATURE OF COMPOUND (ALIPHATIC OR AROMATIC)

To establish the aliphatic or aromatic nature of a compound, it is subjected to ignition test. The organic compound is heated first slowly, and then strongly in a burner flame on a nickel spetula and analysed as follows:

(*a*) **Non-luminous (non-smoky) flame.** Alphatic, containing a low percentage of carbon. Except chloroform, chloral hydrate and ethyl acetate.

(*b*) **Sooty (smoky) flame.** Aromatic compounds or chloroform, choral hydrate, ethyl acetate are indicated.

(*c*) **Non-inflammable.** Halogen-rich-compounds or metal containing compounds.

(*d*) **Residual ash.** Compounds containing a metal.

(*e*) **Charring.** Carbohydrates (odour of burnt sugar), citric acid, tartaric acid and their salts, salts of some acids like succinic, lactic and salicylic.

(*f*) **Violet vopours.** Iodoform.

Caution: The vapours or gases evolved may be poisonous, they should not be inhaled.

Other tests employed for distinction between aromatic and aliphatic compounds are:

(1) *Le Rosen test*. Take about 0.2g (3 to 4 drops if liquid) of organic compound in a boiling tube and add 3-4 drops of formalin (formaldehyde solution) and 5ml of conc. H_2SO_4 shake and heat gently. Appearance of a red, orange, violet or green colour or precipitate indicates aromatic character, if no colour change occurs the compound is aliphatic.

(2) *Nitration.* To a clean and well dried boiling tube add 1 g (or 1 ml of liquid) of organic compound. Add 4ml of nitrating mixture to this and heat the tube carefully for about five minutes. Cool and pour the contents in excess of cold water. If a yellow oily liquid or solid separates the compound is an aromatic otherwise aliphatic.

Caution: While performing this test, one has to be very careful. The boiling tube should be perfectly dry and during boiling process one should not allow even a single drop of water to enter the tube. It will cause an explosion.

(*D*) TEST FOR UNSATURATION

In order to find out if the compound is unsaturated following two tests are commonly applied:

(*i*) **Bromine decolourisation test.** To a solution of 0.1g of the unknown in 2ml of carbon tetrachloride is added dropwise and with shaking a 5 per cent solution of bromine in carbon tetrachloride. The discharge of reddish brown colour of bromine without evolution of hydrogen bromide represents a positive test for unsaturation.

(*ii*) **The Baeyer test.** This test is applied to supplement the bromine decolourisation test for unsaturation.

To a solution of 0.1g of the compound in 2ml of water or ethanol and Baeyer's reagent (dilute alkaline $KMnO_4$ solution) dropwise and with continuous shaking. If the purple colour disappears the compound may be unsaturated. Shake the mixture and continue the addition of potassium permanganate solution until the purple colour persists and allow the solution to stay for 1-2 minutes. If the colour of $KMnO_4$ is discharged again then the compound is positively unsaturated, but if the colour persists the compound may be saturated.

(*E*) ELEMENTAL ANALYSIS

After the observance of physical state, the compound is next subjected to elemental analysis. To determine whether the compound contains nitrogen, halogen or sulphur, the procedure given in Chapter 9 is followed. The presence of carbon in an organic compound is taken as granted while hydrogen is rarely absent. Presence of oxygen is almost certain if (*i*) carbon and hydrogen only have been detected and the substance is soluble in water, (*ii*) carbon, hydrogen and a halogen (but no nitrogen) have been detected, and the substance dissolves freely in cold water.

(*F*) DETECTION OF FUNCTIONAL GROUPS

Depending upon the information gathered in the previous tests, the given compound is subjected to the analysis of functional groups. The nature of the functional groups, mainly depends upon the presence or absence of nitrogen, sulphur or halogens. Therefore, success of the scheme of identification is dependent on the correct elemental analysis.

Organic compounds, based on the elemental analysis can be classed into the following groups:

Sl. No.	*Extra Elements* (N,S,Cl,Br,I)	*Functional Groups*
1.	No extra-element	Acids, alcohols, phenols, aldehydes, ketones, esters, acid, anhydrides, carbohydrates, quinones, ethers and hydrocarbons.
2.	Halogen	Acid halides, halogenohydrocarbons and chloral hydrate.
3.	Nitrogen	Amines, amides, imides, ammonium salts, nitriles, anilides, amino acid, nitrocompounds and uric acid.
4.	Sulphur	Sulphonic acids, alkali bisulphite compounds of aldehydes and ketones.
5.	Nitrogen and Halogen	Salts of amines, nitro amines and amino-carboxylic acids with halogen acids.
6.	Halogen and Sulphur	Aryl sulphonyl chlorides.
7.	Sulphur and Nitrogen	Salts of amines and nitro amines with H_2SO_4, aminoaromatic sulphonic acid and cystine.

(*G*) PREPARATION OF DERIVATIVES

After the functional group in the unknown has been identified, at least one solid derivative and preferably two, should be prepared in order to complete the identification. The requirements of suitable derivatives are:

(*i*) it must be a solid having a simple method of preparation and purification.

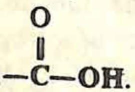
(*ii*) there should be a wide difference (at least 20° C) in the melting point of the original compound and the derivative.

(*iii*) the other homologues of the original compound should also be capable of forming similar derivatives.

Some of the most useful derivatives, for various classes of compounds are given with the analysis of various functional groups in the following discussions.

10.2 CONFIRMATORY TESTS FOR FUNCTIONAL GROUPS

When a given compound does not respond positively to tests for nitrogen, nalogen and sulphur, then the tests for various functional groups should be performed in the following order:

(*a*) **Tests for corboxylic acid group,**  $-\overset{\overset{O}{\|}}{C}-OH$. (*i*) *Bicarbonate test*. Take a saturated solution or sodium bicarbonate in a watch glass and add a few drops of compound if it is liquid, or a pinch if it is solid. Vigorous evolution of CO_2 with brisk effervescence indicates the presence of carboxylic group.

$$R\,COOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow$$

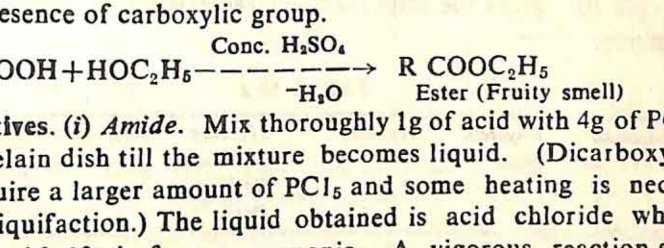
(ii) Acriflavine test. To a mixture of 0.1 per cent acriflavine and 1 per cent potassium chromate solution (2ml each), add a few drops of aqueous solution unknown (if it is liquid it may be used as such) appearance of a yellow or brown-yellow precipitate confirms the presence of $-COOH$ group.

(iii) Ester formation. Heat gently 1 ml of ethanol with 0.5g of the compound (1 ml if liquid) and a few drops of conc. H_2SO_4 for about one minute in a boiling tube. A fruity smell of ester indicates the presence of carboxylic group.

$$RCOOH + HOC_2H_5 \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4} \underset{\text{Ester (Fruity smell)}}{R\,COOC_2H_5}$$

Derivatives. *(i) Amide.* Mix thoroughly 1g of acid with 4g of PCl_5 in a porcelain dish till the mixture becomes liquid. (Dicarboxylic acids require a larger amount of PCl_5 and some heating is necessary for liquifaction.) The liquid obtained is acid chloride which is treated with 10ml of conc. ammonia. A vigorous reaction sets in when the reaction is over stir, cool and filter wash the amide obtained with cold water and then recrystallise from water or alcohol, dry and determine its melting point.

Note. If a solid does not separate on adding ammonia, evaporate the solution to dryness on a water-bath and recrystallise the crude amide from water.

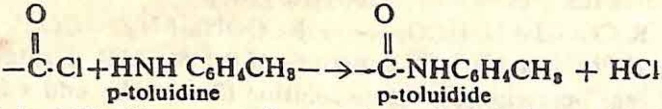


$$-\overset{\overset{\large O}{\|}}{C}-OH + PCl_5 \longrightarrow \underset{\text{(Acid chloride)}}{-\overset{\overset{\large O}{\|}}{C}-Cl} + POCl_3 + HCl$$

$$\underset{\text{Acid Chloride}}{-\overset{\overset{\large O}{\|}}{C}-Cl} + NH_4OH \longrightarrow \underset{\substack{\text{Acid Amide}\\ \text{(Solid)}}}{-\overset{\overset{\large O}{\|}}{C}-NH_2} + HCl + H_2O$$

(ii) Anilide or p-toluidide. Dissolve the acid chloride (prepared as above) in 5ml of acetone and transfer into 100ml conical flask. To this add 1ml of aniline and allow it to stand for five minutes, add 1g of freshly fused sodium acetate. Heat 2-3 minutes on a water-bath, cool and add 5ml dil. HCl. The anilide obtained is filtered, washed with water and recrystallised from alcohol. Dry and determine the melting point.

If in place of aniline, *p*-toluidine is used the product is *p*-toluidide.



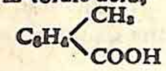
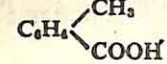
$$-\overset{\overset{O}{\|}}{C}\text{-}Cl + \underset{\text{p-toluidine}}{HNH\,C_6H_4CH_3} \longrightarrow \underset{\text{p-toluidide}}{-\overset{\overset{O}{\|}}{C}\text{-}NHC_6H_4CH_3} + HCl$$

(iii) *Anhydride (in case of succinic and phthalic acids).* Heat about 2g of the acid in a porcelain dish covered with a perforated filter paper on which an inverted funnel is placed. The stem of the funnel is plugged with cotton-wool. Collect the solid anhydride deposited on the inner walls of the funnel and determine the melting point.

Table 10.2 gives the important characteristics of some individual members.

TABLE 10.2

Compound	*Physical state*	*Nature*	*Melting point or Boiling Point °C*	*Derivatives*	*Melting point of derivative °C*
1	2	3	4	5	6
Formic acid, HCOOH	Liquid	aliphatic	B.Pt. 100	Amide Anilide p-toluidide	195 47 53
Acetic acid, CH_3COOH	,,	,,	B. Pt. 118	Amide Anilide p-toluidide	82 115 147
Propionic acid, CH_3CH_2COOH	,,	,,	B. Pt. 140	Amide anilide p-toluidide	79 103 124
Oxalic acid, $\begin{array}{l}COOH\\ \vert \quad .\,2H_2O\\ COOH\end{array}$	Solid	,,	M. Pt. 101	Anilide p-toluidide Urea Oxalate	245 267 171
Malonic Acid, $CH_2\,(COOH)_2$	,,	,,	M. Pt. 133	Amide Anilide p-toluidide	170 225 253
Succinic acid, $\begin{array}{l}CH_2-COOH\\ \vert\\ CH_2-COOH\end{array}$	,,	,,	M. Pt. 185	Amide Anilide p-toluidide Anhydride	260 229 255 119
Benzoic Acid, $C_6H_5\,COOH$	,,	Aromatic	M. Pt. 121	Amide Anilide p-toluidide	129 162 158
O-Toluic acid, $C_6H_4\begin{cases}CH_3\\COOH\end{cases}$	,,	,,	M. Pt. 105	Amide Anilide p-toluidide	143 125 144

1	*2*	*3*	*4*	*5*	*6*
m-toluic acid,  $C_6H_4\left\langle\begin{smallmatrix}CH_3\\ COOH\end{smallmatrix}\right.$	Solid	Aromatic	M. Pt. 111	Amide Anilide p-Toluidide	95 126 118
p-Toluic acid,  $C_6H_4\left\langle\begin{smallmatrix}CH_3\\ COOH\end{smallmatrix}\right.$	,,	,,	M. Pt. 178	Amide Anilide p-Toluidide	159 148 160
Phthalic acid, $C_6H_4(COOH)_2$ O—isomer	,,	,,	M. Pt. 195	Amide Anhydride	220 130

SPECIAL REACTIONS

Formic Acid, HCOOH.

(*i*) *Carbon monoxide test.* Take 1ml of formic acid and 2ml of conc. H_2SO_4 in a test tube and warm gently. Ignite the gas evolved. A pale-blue flame travelling down the test tube indicates carbon monoxide. Dilute solutions of formic acid do not respond to this test.

(*ii*) *Reduction of ammomical silver nitrate.* Formic acid responds positively to the Tollens' reagent test (see test under Aldehydes p. 195).

(*iii*) *Nitroprusside test.* To 1ml of acid in a test-tube add a little $NaHSO_3$, warm and add sodium nitroprusside solution when a greenish blue colour is obtained.

(*iv*) *Reduction of acid permanganate.* Add a few ml of dil. H_2SO_4 to a solution of formic acid, add a dilute. solution of $KMnO_4$ drop by drop. The pink colour of $KMnO_4$ is decolorised, which is hastened by warming.

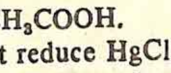
(*v*) *Mercuric chloride test.* Formic acid gives white precipitate of mercurous chloride with mercuric chloride solution. The precipitate being insoluble in dil. HCl. Sometimes the reduction proceeds as far as matallic mercury, which appears as a grey precipitate.

Acetic acid, CH_3COOH.

(*i*) Does not reduce $HgCl_2$, $KMnO_4$ or ammonical $AgNO_3$.

(*ii*) Pleasant fruity odour of methyl and ethyl acetates is characteristic.

Oxalic Acid,



$$\begin{array}{l}COOH\\ \;|\\ COOH.\end{array}\cdot 2H_2O$$

(*i*) *Calcium chloride test.* To 2ml of neutral solution of acid add

$CaCl_2$ solution. A white precipitate, insoluble in acetic acid but soluble in dilute HCl, is obtained.

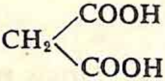
(*ii*) *Reduction of acid permanganate.* Add a few ml of dil. H_2SO_4 to 1ml of a solution of oxalic acid and warm gently. Then, add a dilute solution of $KMnO_4$ drop by drop and note the decolorisation.

(*iii*) *Carbon monoxide test.* On heating with conc. H_2SO_4 gives a mixture of CO and CO_2 which on ignition burns with blue flame.

Propionic Acid, CH_3CH_2COOH.

(*i*) *$FeCl_3$ test.* To 2ml of neutral acid solution add, a few drops of neutral $FeCl_3$ solution. A brownish red colour indicates propionic acid. *The colour goes to amyl alcohol layer if the solution is shaken with it.*

Malonic Acid,

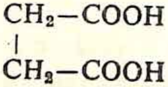


$$CH_2\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix}$$

(*i*) *Fluorescence test.* Mix about 0.2g of acid with 5ml of acetic anhydride and heat. An orange coloured solution with green fluorescence is obtained.

(*ii*) *Formation of tribromoacetic acid.* To a solution of malonic acid, add bromine water. Tribromoacetic acid (m. pt. 135°C), with evolution of Br_2 is formed.

Succinic acid,

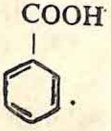


$$\begin{matrix}CH_2-COOH\\ |\\ CH_2-COOH\end{matrix}$$

(*i*) *Fluorescence test.* To 0.2g of acid add 0.5g of resorcinol and 1ml of conc. H_2SO_4 in boiling-tube. Heat until the mixture becomes dark brown, cool and then pour into a beaker containing NaOH solution. An orange green fluorescence is obtained.

(*ii*) *Calcium chloride test.* To 2ml of neutral solution of the acid, add 2ml of $CaCl_2$ solution, shake and boil for 2 minutes. Scratch the sides of the tube, a white precipitate of calcium succinate soluble in acetic acid, is obtained.

Benzoic Acid,



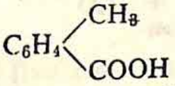
(*i*) *$FeCl_3$ test.* Dissolve 0.5g of acid in dilute ammonium hydroxide, boil off excess of ammonia, and dilute to 20ml. To one part of it add 2 drops of alcoholic ferric chloride, a flesh coloured precipitate of basic ferric benzoate is obtained. On adding dil. HCl, the benzoate is decomposed with the separation of benzoic acid.

To another part add silver nitrate. White precipitate of silver benzoate, soluble in hot water, is produced.

(*ii*) Does not form a phthalein or fluorescein (distinction from phthalic acid).

(*iii*) To 0.2g of acid in a test tube add 2ml of the nitrating mixture. Warm gently for 5-10 minutes, cool and pour in a beaker containing water. A pale yellow solid, mainly m-nitrobenzoic acid (m. pt. 140°C) separates out.

Toluic Acid,

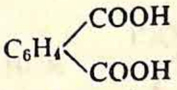


$C_6H_4\begin{cases}CH_3\\COOH\end{cases}$

(*i*) *Alkaline $KMnO_4$ test.* All the o,m & p-toluic acids react with alkaline $KMnO_4$ to give phthalic acid (m. pt. 195°C), isophthalic acid (m pt. 347°C) and terephthalic acid (m.pt. >300°C), respectively.

(*ii*) *Soda-lime test.* When a mixture of acid and soda-lime are heated vapours of toluene are given off which burn with a smoky flame on ignition. All the three isomers respond to this test positively.

Phthalic Acid,



$C_6H_4\begin{cases}COOH\\COOH\end{cases}$

(*i*) *Fluorescence test.* Perform the test as given under succinic acid. A reddish solution having an intense green fluorescence is produced.

(*ii*) *Phthalein reaction.* Fuse together carefully in a dry test-tube, a few crystals of phthalic acid or of a phthalate and an equal quantity of phenol with a few drops of conc. H_2SO_4 cool, dissolve in water, add sodium hydroxide solution in excess, a bright red colour of phenolphthalein in alkaline solution is produced.

(*iii*) *Anhydride.* Prepare anhydride as described under derivatives; *m. pt.* 130°C.

(b) Tests for alcoholic group, —OH. (*i*) *Ceric-ammonium-nitrate test.* To 1ml of the substance add a few drops of ceric ammonium nitrate reagent. Appearance of red colour confirms the presence of alcoholic group.

$$2R\,OH + \underset{\text{cerric amm. nitrate}}{(NH_4)_2\,Ce\,(NO_3)_6} \longrightarrow \underset{\text{Red}}{(ROH)_2\,Ce(NO_3)_4} + 2NH_4NO_3$$

(*ii*) *Sodium test.* To 2ml of unknown add a small piece of sodium metal. A vigorous effervescence due to the evolution of hydrogen indicates the presence of alcoholic hydroxyl group.

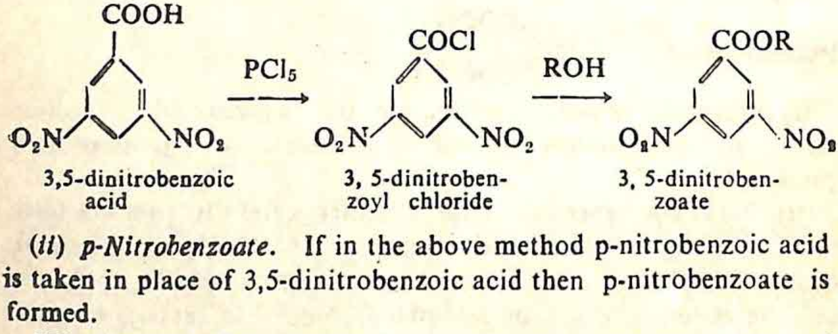
$$2ROH + 2Na \longrightarrow 2R\overset{-}{O}\,\overset{+}{Na} + H_2\uparrow$$

Note. The organic compound should be essentially dried with a little anhydrous calcium or magnesium sulphate before applying the sodium test.

(*iii*) ***Reaction with acetyl chloride.*** To 1ml of the substance add 2-3 drops of acetyl chloride when HCl gas is liberated. If a rod dipped in NH_4OH is brought in contact with the vapours, dense white fumes are produced, according to the following reactions:

$$ROH + CH_3COCl \longrightarrow ROOC\,CH_3 + HCl$$
$$HCl + NH_4OH \longrightarrow \underset{\text{white fumes}}{NH_4Cl} + H_2O$$

Derivatives. (*i*) *3,5-Dinitrobenzoate.* Mix well 0.5g of 3,5 dinitrobenzoic acid with 1g of PCl_5 in a porcelain dish until a semi-solid is obtained. To this add 1ml of alcohol and stir well with a glass rod. Heat on a water-bath until a clear solution is obtained. Allow to stand for five minutes, then add 25ml of 10% Na_2CO_3 solution and stir the contents for about 3 minutes. Filter off the solid ester which separates, recrystallize from alcohol dry and determine the melting point.



3,5-dinitrobenzoic acid

3, 5-dinitrobenzoyl chloride

3, 5-dinitrobenzoate

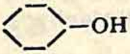
(*ii*) *p-Nitrobenzoate.* If in the above method p-nitrobenzoic acid is taken in place of 3,5-dinitrobenzoic acid then p-nitrobenzoate is formed.

(*iii*) ***Acetates.*** Take 1g of substance in a dry test tube and 1ml of acetyl chloride (or 4ml of acetic anhydride with 2-3 drops of conc. H_2SO_4). Heat the contents by keeping in water bath for 10-15 minutes cool and pour into 10ml water taken in a 100ml beaker. Filter off the derivative formed. Recrystallize from alcohol, dry and determine the melting point.

$$\underset{\text{Acetate}}{ROOC\,CH_3} \xleftarrow[H_2SO_4]{(CH_3CO)_2O} \underset{\text{Alcohol}}{ROH} \xrightarrow{CH_3COCl} \underset{\text{Acetate}}{ROOC\,CH_3}$$

Some individual members alongwith their derivatives and important properties are listed in the Table 10.3.

TABLE 10.3

Compound	*Physical State*	*Nature*	*Melting or Boiling Point °C*	*Derivatives*	*Melting Point of Derivative °C*
Methyl Alcohol, CH_3OH	Liquid	Aliphatic	B. Pt. 64.5	3, 5-Dinitrobenzoate	109
				p-nitrobenzoate	96
Ethyl alcohol, CH_3CH_2OH	,,	,,	B. Pt. 78	3, 5-Dinitrobenzoate	94
				p-nitrobenzoate	57
Isopropyl alcohol, $(CH_3)_2$ CHOH	,,	,,	B. Pt. 82	3, 5-Dinitrobenzoate	122
				p-nitrobenzoate	110
n-Propyl alcohol, $CH_3CH_2CH_2OH$	,,	,,	B. Pt. 97	3, 5-Dinitrobenzoate	75
				p-nitrobenzoate	35
Iso-butyl alcohol, $(CH_3)_2$ CH CH_2 OH	,,	,,	B. Pt. 108	3, 5-dinitrobenzoate	88
				p-nitrobenzoate	108
n-Butyl alcohol, $CH_3CH_2CH_2$ CH_2OH	,,	,,	B. Pt. 118	3, 5-Dinitrobenzoate	64
				p-nitrobenzoate	36
Cyclohexanol 	,,	,,	B. Pt. 161	3, 5-Dinitrobenzoate	113
				p-nitrobenzoate	50
Glycerol CH_2OH | CH OH | CH_2OH	,,	,,	B. Pt. 290 (decomposes)	p-nitrobenzoate	188
				tribenzoate	72
Benzyl alcohol $C_6H_5CH_2OH$	,,	Aromatic	B. Pt. 205	3, 5-Dinitrobenzoate	113
				p-nitrobenzoate	86

SPECIAL REACTIONS

Methyl alcohol, CH_3OH.

(*i*) *Methyl salicylate test.* In a dry test tube, heat 1ml of methyl alcohol with 0.5g of salicylic acid and 5-6 drops of conc. H_2SO_4 for 2 minutes. Cool, pour into a few ml of cold water in a boiling tube, and shake. A characteristic smell of oil of winter green (like iodex) due to the formation of methyl salicylate, is produced.

(*ii*) *Formaldehyde test.* Heat a copper wire to redness and plunge it while hot into a test tube containing 1ml of methyl alcohol. Pungent smell if formaldehyde is produced. To this add 2 drops of an aqueous solution of resorcinol (0.5%) and pour 2ml of conc. H_2SO_4 along the side of the test-tube. A dull violet ring is formed at the junction of two liquids and a white precipitate changing into red violet is formed in the aqueous solution above the ring.

Note. Formaldehyde is also formed by adding $K_2Cr_2O_7$ and H_2SO_4 to methanol in cold.

Ethyl alcohol, C_2H_5OH.

(*i*) *Ethyl acetate test*. To 2ml substance in a test-tube add 2ml of glacial acetic acid and a few drops of conc. H_2SO_4. Heat gently for about 1 minute, cool and pour into a few ml of water in a boiling-tube. A fruity smell of ethyl acetate is produced.

(*ii*) *Iodoform test*. To 1ml of ethyl alcohol in a test-tube add 3-4 drops of iodine solution and then sodium hydroxide solution drop by drop. Warm gently, fine yellow crystals of iodoform having characteristic smell are formed.

(*iii*) *Formation of acetaldehyde*. To 1ml of dilute potassium dichromate solution add a drop or two of conc. H_2SO_4 and then add 5 drops of ethyl alcohol. Heat gently and note the change in colour of the solution to green and the characteristic smell of acetaldehyde.

Isopropyl alcohol, $(CH_3)_2$ CHOH.

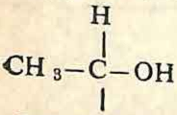
(*i*) *Isopropyl alcohol responds to iodoform test*. (see under ethyl alcohol)

(*ii*) *Formation of acetone*. On oxidation with $K_2Cr_2O_7$ and H_2SO_4, isopropyl alcohol yields acetone having characteristic sweet smell.

n-Propyl alcohol, $CH_3CH_2CH_2$ OH.

(*i*) *Oxidation test*. Oxidation of substance with $K_2Cr_2O_7$ and H_2SO_4 yields propionaldehyde having pungent smell.

(*ii*) Does not respond to iodoform test due to lack of



$CH_3-\overset{\overset{H}{|}}{\underset{|}{C}}-OH$ structure.

Isobutyl alcohol, $(CH_3)_2$ $CHCH_2OH$.

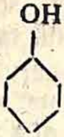
(*i*) *Responds to iodoform test*. (see under ethyl alcohol)

(*ii*) Heat 0.5ml of the alcohol with a trace of $K_2Cr_2O_7$ and a few drops of conc. H_2SO_4. Place a paper moistened with ammonical silver nitrate near the mouth of the test-tube. A black stain is not obtained on the paper.

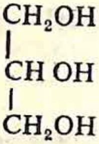
n-Butyl alcohol, $CH_3CH_2CH_2$ CH_2OH

(*i*) It does not give iodoform test.

(*ii*) Apply test (*iii*) under **isobutyl** alcohol, a black stain on the paper confirms n-butyl alcohol.

Cyclo-hexanol, 

(*i*) *Oxidation test.* To 1ml of the substance add a few drops of conc. HNO_3 in a boiling-tube and heat. Cool when crystals of adipic acid (m.pt. 151°C) separate.

Glycerol, 

$$\begin{array}{l} CH_2OH \\ | \\ CH\,OH \\ | \\ CH_2OH \end{array}$$

(*i*) *Acrolein test.* Heat 0.5 ml glycerol with about 1g of finely powdered $KHSO_4$. An irritating pungent smell of acrolein is observed (smell cautiously).

(*ii*) *Tollens' test.* To 2ml Tollens' reagent in a test tube add 2-3 drops of substance keep the test-tube in boiling water without disturbing for five minutes. A shining silver mirror deposits on the walls of test-tube.

(*iii*) Heat 2 drops of glycerol with 2 drops of phenol and 2 drops of conc. H_2SO_4 in a test-tube. Cool, add 10 ml water and NH_4OH solution. A red colour is produced.

(*iv*) To 5ml of borax solution add a drop of phenolphthalein solution, a pink colour is produced. **Add 2 or 3 drops of glycerol** and shake, pink colour disappears. **The colour reappears on heating** the mixture and on cooling vanishes again.

Benzyl alcohol, $C_6H_5CH_2OH$.

(*i*) *Formation of benzaldehyde.* To 1-2 drops of substance add 2ml dilute HNO_3 and keep the test-tube in boiling water for 2-5 minutes. A pale yellow emulsion along with strong bitter almonds smell due to formation of benzaldehyde is observed.

(*ii*) *Oxidation to benzoic acid.* Heat 0.5 ml of benzyl alcohol with 0.2g of $KMnO_4$ in aqueous solution for five minutes. Cool, when crystals of benzoic acid (m.pt. 121°C) separate out.

(*iii*) Action of sulphuric acid. To 0.5ml of the substance, and 0.5ml of conc. H_2SO_4 and shake the mixture. Heat is evolved and a white gelatinous polymer gradually separates. The reaction becomes fast on heating and the product darkens.

(c) **Tests for Phenolic Group,** (C_6H_5-OH). **Phenols are colour-**

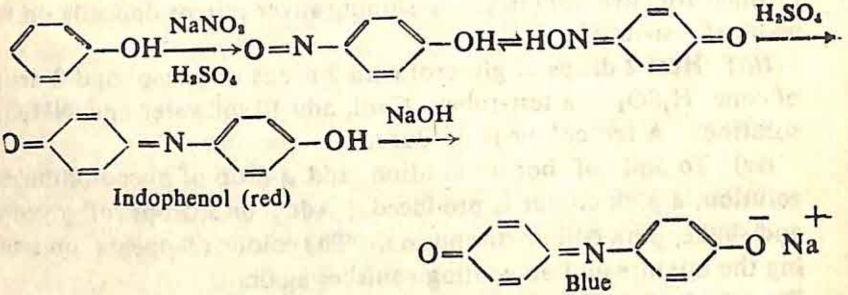
less compounds but attain colour due to oxidation. They are soluble in 5% NaOH solution and insoluble in 5% sodium carbonate solution. The presence of phenolic group in the molecule is determined by the following tests.

(*i*) *Ferric chloride test*. To one ml of dilute solution (0.2% in water or ethanol) of phenol add only 2 drops of a 5% neutral $FeCl_3$ solution. A violet, green, pink or wine-red colour indicates the presence of phenolic group in the molecule. The coloration is said to be due to the formation of complex ion,

$$6C_6H_5OH + FeCl_3 \longrightarrow \underset{\substack{\text{Complex ion} \\ \text{(coloured)}}}{[Fe(O-C_6H_5)_6]^{3-}} + 3HCl + 3H^+$$

The reaction takes place in polar solvents.

(*ii*) *Liebermann reaction*. Dissolve 0.1g of unknown in 1ml of conc. H_2SO_4 in a dry test tube and add a few crystals of $NaNO_2$. A blue-green or blue-violet colour is immediately formed which changes to red on dilution. Further, on adding NaOH solution a blue colour is again formed. Only those phenols which possess a free para position respond to this test.



(*iii*) *Phthalein test*. Introduce 0.2g of the unknown and phthalic anhydride alongwith 2 drops of conc. H_2SO_4 in a test-tube and heat for one minute. Cool and pour carefully the contents to a 10% NaOH solution taken in a beaker. Characteristic colours are obtained.

Phenol	Red
catechol, hydroquinoue	Blue
α-and β-Naphthols	Light green
p-Cresol	Coloureless.

Derivatives. (*i*) *Benzoates*. Dissolve 1g of the phenol in about 15ml of 10% NaOH solution contained in a 100ml round-bottomed flask. Add 5ml of acetone and then 5ml of benzoyl chloride and cork the flask securely and shake vigorously for at least 10 minutes, until the odour of benzoyl chloride disappears. Filter at pump, wash the solid first with dilute HCl and then with cold water.

Recrystallize from alcohol, acetone or benzene and determine the melting point.

$$\underset{\text{Phenol}}{ArOH}+\underset{\substack{\text{Benzoyl}\\\text{chloride}}}{C_6H_5COCl}\longrightarrow \underset{\text{Benzoate}}{ArO.\ OCC_6H_5}+HCl.$$

(*ii*) *Acetates.* To one ml or 1g of substance in a dry test-tube add 3ml of acetic anhydride and 1 drop of conc. H_2SO_4. Shake the contents for two minutes and then pour it into 10ml water in a porcelain dish and stir until the oily liquid solidifies. Filter and wash the solid with cold water. Dry and recrystallize from acetone. Dry and determine the melting point.

$$ArOH+CH_3COCl\longrightarrow \underset{\text{Acetate}}{ArO.\ OC\ CH_3}+HCl$$

SPECIAL REACTIONS

Phenol, C_6H_5OH. **B. Pt.** 182°C.

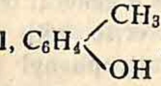
(1) Gives violet colour with neutral $FeCl_3$

(2) Gives pink-red colour in phthalein test

(3) Responds positively to Libermann's test.

Derivatives. (*i*) *Benzoate, m.pt.*=69°C.

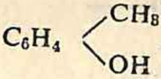
(*ii*) *Tribromophenol.* Dissolve 0.5g of phenol in 10ml of water and add bromine water to the solution until the colour of the solution indicates that a slight excess of bromine is present. Add a little sodium bisulphite solution to remove the excess bromine. Filter the precipitate of 2,4,6—tribromophenol, wash with water, and recrystallize it from hot ethyl alcohol. Melting point=96°C.

O-crestol, 
$C_6H_4\left\langle\begin{matrix}CH_3\\OH\end{matrix}\right.$, B. Pt. 191°C.

(1) Responds to Phthalein test and Libermann reaction.

Derivatives. (*i*) p-Nitrobenzoate=M. Pt. 94°C

(*ii*) 3, 5-dinitrobenzoate=M. Pt.=138°C

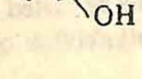
m-Cresol, 
$C_6H_4\left\langle\begin{matrix}CH_3\\OH\end{matrix}\right.$,B. Pt. 202°C.

(*i*) Responds to Libermann reaction.

(*ii*) Imparts a blue-violet colour in phthalein test.

Derivatives. (*i*) Benzoate=M. Pt. 55°C

(*ii*) p-Nitrobenzoate=M. Pt. 90°C.

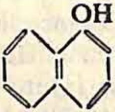
p-Cresol, 
$C_6H_4\left\langle\begin{matrix}CH_3\\OH\end{matrix}\right.$,B. Pt. 202°C.

(*i*) Gives blue colour with aq. $FeCl_3$ solution.

(*ii*) Gives red colour when Libermann reaction is applied.

Derivatives. (*i*) Benzoate=M.Pt. 71°C

(*ii*) p-Nitrobenzoate=M. Pt. 98°C

α—Naphthol, 

, M.Pt. 94°C.

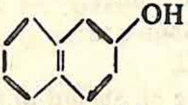
(*i*) *$FeCl_3$ test.* Gives a white ppt. with $FeCl_3$ solution in water.

(*ii*) To a small amount of compound add 2ml of NaOH solution and a drop of CCl_4 and a pinch of copper powder. Warm gently, when a blue colour appears.

(*iii*) *Titanic acid test.* Heat a small amount of substance with titanic acid and conc. H_2SO_4. Appearance of green colour confirms α-Naphthol.

Derivatives. (*i*) Benzoate=M. Pt. 56°C

(*ii*) p-Nitrobenzoate=M. Pt. 143°C

β-Naphthol, 

, M. Pt. 123°C.

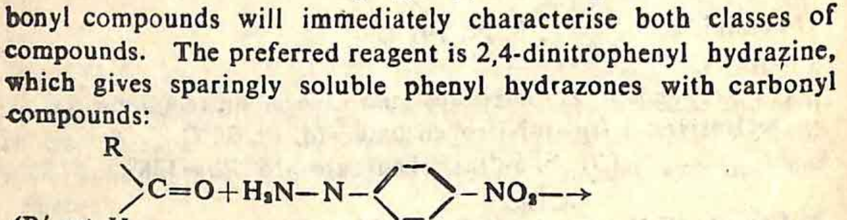
(*i*) With titanic acid in conc. H_2SO_4 gives a red colour.

(*ii*) Does not respond to test No. (ii) as given under **α-Naphthol.**

Derivatives. (*i*) Benzoate=M. Pt. 107°C

(*ii*) p-Nitrobenzoate=M. Pt. 169°C

(d) Tests for carbonyl group, >C=O. Both aldehydes and ketones contain the carbonyl group, hence a general test for carbonyl compounds will immediately characterise both classes of compounds. The preferred reagent is 2,4-dinitrophenyl hydrazine, which gives sparingly soluble phenyl hydrazones with carbonyl compounds:

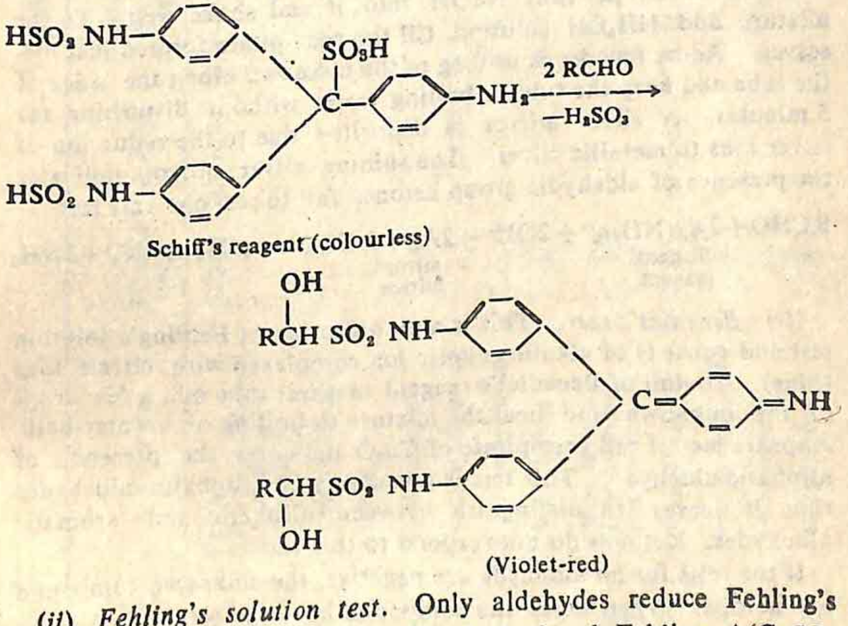


2, 4-Dinitrophenyl hydrazine (DNP) Test. To 3ml of 2,4-DNP reagent add 2 drops or 0.1g of the substance to be tested and shake vigorously. If no precipitate forms immediately allow to stand for 5-10 minutes. A bright orange crystalline precipitate separates out in the case of carbonyl compounds only. The high reactivity of the compounds with this reagent is due to the character of the carbonyl group.

If the unknown compound gives a positive test with 2,4—DNP reagent, it then becomes necessary to decide whether it is an aldehyde or a ketone.

Differentiation between aldehydes ($R-\overset{\overset{O}{\|}}{C}-H$) and ketones ($R-\overset{\overset{O}{\|}}{C}-R$).

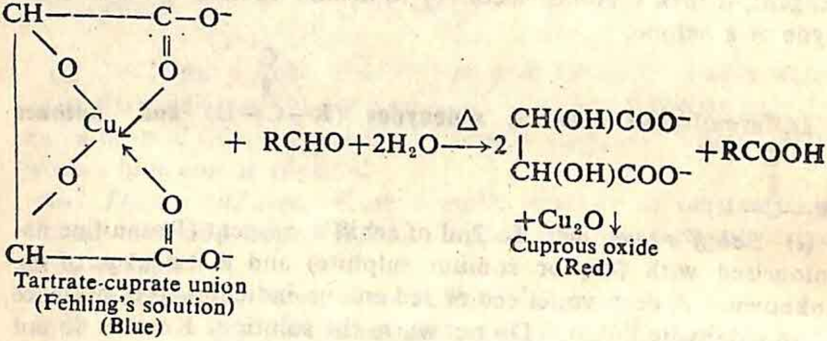
(*i*) *Schiff's reaction.* To 2ml of schiff's reagent (Rosaniline decolourised with SO_2 or sodium sulphite) and a few drops of the unknown. A deep voilet-red or red colour indicates the presence of an aldehydic group. Do not warm the solution. Ketones do not respond to this test. A number of aromatic aldehydes (e.g., vanillin) give a negative result.



Schiff's reagent (colourless)

(Violet-red)

(*ii*) *Fehling's solution test.* Only aldehydes reduce Fehling's solution to red cuprous oxide. Mix 1ml of each Fehling A($CuSO_4$ in water with a few drops of acetic acid) and Fehling B (Rochelle salt with NaOH solution) solutions in a test-tube. To this add 2-3 drops of substance and boil for 5-10 minutes on a water-bath. The blue colour of Fehling's solution slowly fades away and a reddish-brown precipitate of Cu_2O is obtained indicating the presence of aldehydic group. This test is positive for aliphatic aldehydes, but is usually indecisive for aromatic aldehydes.



(iii) Tollens' test. Clean a test tube by boiling conc. HNO_3 in it. Then introduce 1m of freshly prepared 10 per cent $AgNO_3$ solution and 1ml of 10 per cent NaOH into it and shake well. To the mixture add NH_4OH solution till the precipitate formed just dissolves. Add a few drops or 0.1g of the unknown along the sides of the tube and keep the tube in boiling water without disturbing for 5 minutes. A silver mirror is deposited due to the reduction of silver ions to metallic silver. The shining silver mirror indicates the presence of aldehydic group ketones fail to respond this test

$$RCHO+\underset{\substack{\text{Tollens'}\\\text{reagent}}}{2Ag(NH_3)_2^+}+2OH^-\rightarrow\underset{\substack{\text{silver}\\\text{mirror}}}{2Ag}+RCOO^-+NH_4^++H_2O+3NH_3$$

(iv) Benedict's test. This is a modification of Fehling's solution test and consists of alkaline cupric ion complexed with citrate ions (blue). To 4ml of Benedict's reagent in a test tube add a few drops of the unknown and heat the mixture to boiling on a water-bath. Appearance of red precipitate of Cu_2O indicates the presence of aliphatic aldehyde. This test is given only by aliphatic aldehydes thus it serves to distinguish between aliphatic and aromatic aldehydes. Ketones do not respond to this test.

If the tests for an aldehyde are negative, the unknown compound is a ketone. When once the compound has been established as an aldehyde or ketone, it is permissible to refer to Table 10.4 and test for individual compounds.

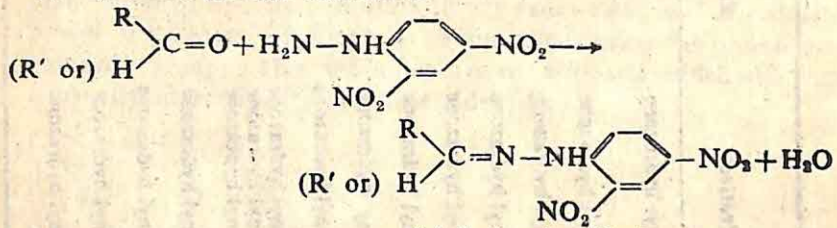
Derivatives. Aldehydes and ketones react with similar reagents

TABLE 10.4

Sl. No.	*Compound*	*Physical state*	*Nature*	*Melting Point or Boiling °C*	*Derivatives*	*Melting point of derivatives °C*
1.	Formalin (40% aq. solution of formaldehyde)	Liquid	Aliphatic	B. Pt. 98	2,4-Dinitrophenyl-hydrozone	166
					Semicarbazone	169
2.	Acetaldehyde	,,	,,	B. Pt. 21	2,4-Dinitrophenyl hydrazone	168
					Semicarbazone	163
3.	Propionaldehyde	,,	,,	B. Pt. 49	2,4-Dinitrophenyl hydrazone	155
					Semicarbazone	89
4.	Acetone	,,	,,	B. Pt. 56	2,4-Dinitrophenyl hydrazone	128
					Semicarbazone	190
5.	Isobutyraldehyde	,,	,,	B. Pt. 64	2,4-Dinitrophenyl hydrazone	187
					Semicarbazone	126
6.	n-Butyraldehyde	,,	,,	B. Pt. 75	2,4-Dinitrophenyl hydrazone	123
					Semicarbazone	106
7.	Ethyl methyl ketone	,,	,,	B. Pt. 80	2,4-dinitrophenyl hydrazone	111
					Semicarbazone	146
8.	Diethyl ketone	,,	,,	B. Pt. 102	2,4-Dinitrophenyl hydrazone	156
					Semicarbazone	139
9.	Acetyl acetone	,,	,,	B. Pt. 139	2,4-Dinitrophenyl hydrazone	209
10.	Cyclopentanone	,,	,,	B. Pt. 130	2,4-Dinitrophenyl hydrazone	146
11.	Cyclohexanone	,,	,,	B. Pt. 156	2,4-Dinitrophenyl hydrazone	162
					Semicarbazone	167
12.	Benzaldehyde	,,	Aromatic	B. Pt. 179	2,4-Dinitrophenyl hydrazone	237
					Semicarbazone	224
13.	Phenylacetaldehyde	,,	,,	B. Pt. 193	2,4-Dinitrophenyl hydrazone	121
					Semicarbazone	153
14.	Acetophenone	,,	,,	B. Pt. 202	2,4-Dinitrophenyl hydrazone	250
					Semicarbazone	199
15.	Benzophenone	Solid	,,	M. Pt. 49	2,4-Dinitrophenyl hydrazone	238
					Semicarbazone	165

to form crystalline solids.

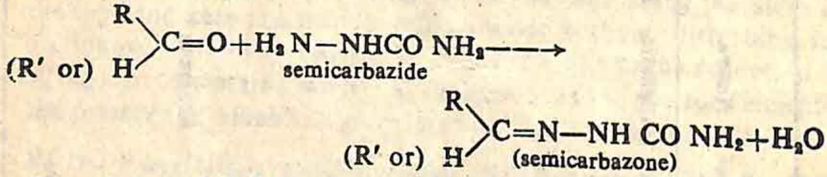
(*i*) *2,4-Dinitrophenyl hydrazone.*



2,4-dinitro phenyl hydrazone

Procedure. Dissolve 0.1g of 2,4-dinitrophenyl hydrazine in 10ml of methanol in an Erlenmeyer flask. To this add 5 drops of conc. HCl and warm to complete the solution. Cool this solution and add to it 0.5ml of substance and shake vigorously. The coloured 2,4-dinitrophenyl hydrazone separates out almot immediately. If the precipitate does not come out immediately then warm in a water-bath for 1-2 minutes and then allow to stand for 15-30 minutes at room temperature till the coloured precipitate is formed. Filter, wash the precipitate with water and recrystallize from aqueous ethanol. Dry and determine the melting point.

(*ii*) *Semi carbazones*. These often form readily in cold and have sharp melting points.

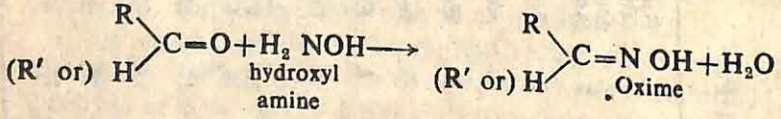


$$\begin{matrix}R\\(R' \text{ or}) H\end{matrix}\!\!>C=O+\underset{\text{semicarbazide}}{H_2N-NHCO\,NH_2}\longrightarrow \begin{matrix}R\\(R' \text{ or}) H\end{matrix}\!\!>\underset{\text{(semicarbazone)}}{C=N-NH\,CO\,NH_2}+H_2O$$

Procedure. Add 0.5g of semicarbazide hydrochloride to 5ml of water, add 0.5g of anhydrous sodium acetate and warm gently until a clear solution is obtained. To this add 0.5ml of substance in 2-3ml of ethanol, and warm on a water-bath. The semicarbazone crystallizes readily, wash with water and recrystallize from ethanol dry and take the melting point.

Many semicarbazones separate when the cold reaction-mixture is set aside for a short time.

(*iii*) *Oximes*



$$\begin{matrix}R\\(R' \text{ or}) H\end{matrix}\!\!>C=O+\underset{\substack{\text{hydroxyl}\\\text{amine}}}{H_2\,NOH}\longrightarrow \begin{matrix}R\\(R' \text{ or}) H\end{matrix}\!\!>\underset{\text{Oxime}}{C=N\,OH}+H_2O$$

Procedure. Dissolve 0.5g of substance in 2ml of alcohol in a test-tube. To this add a solution of 0.5g hydroxylamine hydrochloride and 1g of crystallized sodium acetate dissolved in 2ml of water. Allow the test tube to stand in boiling water for 20-30 minutes. Cool and filter the solid so formed with cold water and recrystallize from alcohol, dry and determine the melting point.

SPECIAL REACTIONS

Acetaldehyde, CH_3CHO.

1. It reduces Fehling's solution and Tollens' reagent.

2. To 2ml of the aqueous solution of acetaldehyde add 2ml of aqueous sodium nitroprusside solution and a few drops of NaOH, when a deep wine-red colour is produced.

3. To 2ml of aqueous solution of the substance add 2ml of 20% KOH solution and boil for one minute. The solution becomes yellow and finally a yellow precipitate changing to orange having disagreeable smell.

Acetone, CH_3COCH_3.

1. To one ml of aqueous solution of the substance add a few drops of sodium nitroprusside and NaOH solution a red colour appears.

2. *Iodoform test*. To 0.5ml of the substance add five drops of iodine solution and then NaOH solution drop by drop. Warm it till the brown colour of iodine disappears, formation of a yellow precipitate of iodoform having characteristic hospital like smell confirms methyl ketone.

Methyl ethyl ketone, $CH_3COC_2H_5$.

Responds to iodoform test.

Benzaldehyde, C_6H_5CHO.

Immiscible and heavier than water having bitter almonds smell.

1. Heat 0.5ml of the substance with 2ml of alkaline $KMnO_4$ for five minutes. Filter and acidify the filtrate with HCl. A white precipitate of benzoic acid is obtained.

2. It does not reduce Fehling's solution.

3. It reduces Tollens' reagent very slowly and a grey precipitate is obtained.

Acetophenone, $CH_3COC_6H_5$.

1. Responds to iodoform test.

2. Produces orange colour when dissolved in conc. H_2SO_4.

3. Gives white precipitate of benzoic acid when oxidised by alkaline $KMnO_4$.

Benzophenone, $C_6H_5COC_6H_5$.

Colourless crystalline solid insoluble in water.

1. Gives a yellow colour when dissolved in conc. H_2SO_4.

2. Fusion of the substance with sodium produces deep blue colour.

(*e*) **Tests for Carbohydrates, $C_x(H_2O)_y$.** Molisch's Test. To 5mg of the substance in 0.5ml of water add 2-5 drops of Molisch's reagent (a 10% solution of α-naphthol in alcohol) and shake. Pour 2ml of conc. H_2SO_4 down the side of the inclined tube carefully, so that the acid forms a layer beneath the aqueous solution without mixing with it and allow to stand for one minute. If a deepviolet ring is obtained at the junction of the two liquids and on shaking the whole mixture becomes violet-red, the original compound is a carbohydrate.

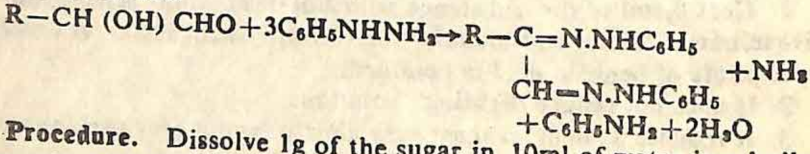
Differentiation between Monosaccharides and disaccharides. **Barfoed's reaction.** To 2ml of Barfoed's reagent add 2ml of the aqueous solution of the compound (2%) and heat the test tube by keeping it in boiling water. If red cuprous oxide is formed within 2 minutes, a monosaccharide is present. Disaccharides on prolonged heating (about 10 minutes) may also cause reduction, owing to partial hydrolysis to monoses.

Monosaccharides and some oligosaccharides reduce Fehling's solution and Tollens' reagent, also they react with phenylhydrazine to produce osazones.

Derivatives. (*i*) Oximes see under carbonyl compounds (p. 197).

(*ii*) Acetates. Take 1g of the substance in a 50ml round bottomed flask and add 10ml acetic anhydride and 1g fused sodium acetate. Boil the contents for fifteen minutes. Cool and pour the contents in cold water taken in a beaker. Filter the solid obtained, wash with cold water, recrystallize from alcohol, dry and determine the meting point.

(*iii*) Osazones.



$$R-CH(OH)CHO+3C_6H_5NHNH_2 \rightarrow \begin{array}{l} R-C=N.NHC_6H_5 \\ \quad | \\ \quad CH=N.NHC_6H_5 \end{array} +NH_3 +C_6H_5NH_2+2H_2O$$

Procedure. Dissolve 1g of the sugar in 10ml of water in a boiling tube, add 2.5ml of phenylhydrazine and 3ml of glacial acetic acid. Mix well, cork the tube, loosely (preferably with cotton plug) and place in a beaker of boiling water. Note the time of immersion and the time when osazone first separates as yellow crystals. Shake the tube occasionally (without removing it from boiling water) in order to prevent supersaturation. Filter, wash with water, recrystallize from hot water or 60% alcohol. Dry and determine the melting point.

Note: Monosaccharides give osazone at 100°C within 20 minutes. The disaccharides, maltose and lactose give no osazone at 100°C even after two hours, but osazones are obtained on cooling after 10-15 minutes heating. With sucrose an osazone commences to separate after about 30 minutes, due to gradual hydrolysis into glucose and fructose, but no osazone is produced on cooling after heating for 10-15 minutes.

TABLE 10.5

Sl. No.	*Compound*	*Physical State*	*Melting point °C*	*Derivatives*	*Melting point of derivative °C*
1.	D-Glucose (hydrated)	Solid	90	Phenylosazone (formed in 5 minutes) Oxime	205 137
2.	D-Glucose (Dextrose)	,,	146	Oxime	137
3.	D-Fructose	,,	95-105	Phenyl osazone (formed in 2 minutes) Oxime	205 118
4.	Maltose	,,	100	Phenyl osazone (formed in one hour)	205
5.	d-lactose (hydrated)	,,	203	Phenyl osazone (formed in 90 minutes) Octa-acetate	208 152
6.	Lactose (anhydrous)	,,	223	Phenyl osazone (formed in 90 minutes) Octa-acetate	208 152
7.	Sucrose	,,	185	Octa-acetate	69
8.	Starch	,,	Decomposes without melting	—	—

SPECIFIC REACTIONS

D-Glucose, $CH_2OH(CHOH)_4CHO$.

White crystalline solid soluble in water and hot alcohol. Insoluble in benzene and ether.

(1) Reduces Tollens' reagent, Fehling's solution and Barfoed's reagent.

(2) Reduces Benedicts solution to orange red precipitate.

(3) Take 2ml of the aqueous solution of glucose in a test tube and add 1g of lead acetate to it boil and add 5ml of dilute NH_4OH and boil the mixture again for one minute. Appearance of rose-pink colour indicates glucose.

Fructose, $CH_2OH\ (CHOH)_3\ COCH_2OH$.

White solid soluble in water but insoluble in alcohol, benzene and ether.

1. Add a small amount of substance to 2ml ammonium molybdate solution. A blue colour confirms fructose.

2. To 2ml of the aqueous solution of sugar in a test-tube add an equal volume of conc. HCl and 0.1g of resorcinol. Warm the tube in a beaker of boiling water for 2 minutes. Production of a deep red colour followed by a precipitate indicates fructose. Apply this test for the distinction from glucose.

3. It reduces Fehling's solution even in cold and Barfoed's reagent on warming.

Sucrose (Cane-sugar), $C_{12}H_{22}O_{11}$.

White crystalline solid soluble in cold water, sparingly soluble in alcohol and insoluble in ether and benzene.

(1) It does not react with Fehling's solution. After its hydrolysis with dilute HCl it reduces Fehling's solution.

(2) It produces a violet colour when heated with cobalt nitrate and NaOH solution.

(3) To 2ml of aqueous solution of substance add a pinch of resorcinol and 2ml conc. HCl. Boil for 2 minutes when deep wine red colour is obtained.

Starch, $(C_6H_{10}O_5)_n.\ H_2O$.

White amorphous powder insoluble in cold water but dissolves in boiling water.

1. It does not respond to Fehling's solution test.

2. When a few drops of iodine solution are added to aqueous solution of substance a blue colour is formed.

(*f*) **Tests for Hydrocarbons.** Hydrocarbons are neutral and do not contain any functional group. They are insoluble in water but dissolve in many organic solvents. Due to lack of reactivity their identification is based mainly upon determination of their melting or boiling points and derivatives.

The following two colour tests can be applied for their identification.

(1) *Formalin test.* To 2 drops of the unknown in CCl_4 add a mixture of 2 drops of formalin and 2ml of conc. H_2SO_4. Note the appearance of colour.

Benzene, Toluene, Diphenyl and Naphthalene.	Dark red colour with black precipitate.
O-Xylene.	Dark brown precipitate.
m-Xylene and p-Xylene.	Violet colour with black precipitate.

Anthracene	Dark yellow colour with black-precipitate.

This being a sensitive test results in the formation of resinous substances.

(2) *Aluminium chloride test*. To 0.1g of the unknwon in 1ml of chloroform add a pinch of anhydrous $AlCl_3$ with a spatula along the sides of the test tube and note the colour.

Benzene	$AlCl_3$ crystals become yellow but turn dark orange within a few minutes. The chloroform layer is colourless.
Toluene	Crystals turn orange and the chloroform layer turns yellow on keeping.
O-Xylene	Orange colour, Chloroform layer initially colourless but turns yellow on keeping.
m-Xylene	Orange colour, chloroform layer colourless.
p-Xylene	Dark red colour, chloroform layer colourless.
Diphenyl	Dark green colour, chloroform layer colourless.
Naphthalene	Green colour turns blue on keeping.
Phenanthrene	Purple colour.
Anthracene	Light yellow colour, chloroform layer colourless.

TABLE 10.6

Sl. No.	*Compound*	*Physical state*	*Nature*	*Melting point or Boiling point °C*	*Derivatives*	*Melting point of derivative °C*
1.	Benzene	Liquid	Aromatic	B. Pt. 80	m-dinitrobenzene	90
2.	Toluene	,,	,,	110	2,4-Dinitrotoluene 2,4,6-Trinitrotoluene	71 82
3.	O-Xylene	,,	,,	144	Phthalic acid	195
4.	m-Xylene	,,	,,	139	2,4,6-Trinitro-m-Xylene	182
5.	p-Xylene	,,	,,	138	2,3,5-Trinitro-p-Xylene Bromo-p-xylene	139 144
6.	Diphenyl	Solid	,,	M. Pt. 70	p,p'-Dinitro-Diphenyl p,p'-Dibromo Diphnyl	234 164
7.	Naphthalene	,,	,,	80	Picrate	150
8.	Phenanthrene	,,	,,	100	Picrate	143
9.	Anthracene	,,	,,	216	Picrate	138

10.3 COMPOUNDS CONTAINING NITROGEN AS AN EXTRA-ELEMENT

If the compound contains nitrogen then test for following functional groups:

(a) Tests for amines. Determine whether the amine is primary, secondary or tertiary by application of the Hinsberg reaction.

Hinsberg reaction. Introduce 0.1g or 3 drops of the unknown into a test tube and add 0.2g of p-toluene sulphonyl chloride and 5ml of 10% NaOH solution. Shake vigorously for five minutes. If no reaction appears to occur, heat the reaction mixture on a water bath for 2 minutes and cool in ice. On cooling, if no solid separates out than the substance is probably a tertiary amine. If a precipitate appears in the alkaline medium add 5ml of water and shake. If the precipitate does not dissolve it indicates a secondary amine. If the solution is clear acidify with dil. HCl. Appearance of a precipitate indicates primary amine.

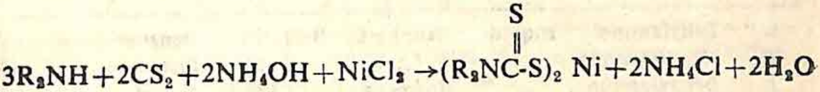
If the Hinsberg test indicates that the amine is primary, confirm the result by applying the Carbylamine test.

Carbylamine test. Place a small amount of the amine in a test tube and dissolve in alcoholic NaOH. Add a few drops of chloroform and warm the mixture gently. An offensive smell of isocyanide (carbylamine) indicates primary amine.

If this test is also positive, conduct the Diazotization and coupling test to determine whether the amine is a primary aliphatic or aromatic one.

Diazotization and coupling test. Dissolve 1g of the unknown in 8ml of a solution of HCl prepared by adding 3ml of commercial acid to 5ml of water. Cool the solution of the amine hydrochloride to 0-5°C in an ice-bath, and slowly add, with shaking the reaction mixture, a solution of 1g of $NaNO_2$ in 5ml of water. During the addition of the sodium nitrite solution, place a drop of the reaction mixture on starch iodide paper from time to time, when a blue colour appears discontinue the addition. If there is no apparant reaction, place 2ml of the solution in a clean test-tube and warm it gently. Note whether a reaction occurs. Add another 2ml portion of the cold amine hydrochloride sodium nitrite solution to a solution of 0.1g of β-naphthol in 7ml of 3% sodium hydroxide solution. Note whether formation of a yellow, orange or red precipitate occurs. Formation of an azo-dye, confirms a primary aromatic amine.

Secondary amine. The presence of a secondary amine as indicated by the Hinsberg test can be confirmed as follows: Dissolve 0.1g of nickel chloride hexahydrate in 20ml of water and then add sufficient carbon disulphide such that a small globule remains undissolved after the mixture has been shaken vigorously. To one ml of this reagent add 1ml of concentrated NH_4OH, and then solution of 0.1g of the unknown in 5ml of water, to which a drop or two of conc. HCl has been added, if necessary, to complete the dissolution of the amine. Shake, a precipitate confirms secondary amine.



$$3R_2NH+2CS_2+2NH_4OH+NiCl_2 \rightarrow (R_2N\overset{\overset{S}{\|}}{C}\text{-}S)_2\,Ni+2NH_4Cl+2H_2O$$

Note. This test is very sensitive one for secondary amines, it should be kept in mind that some primary and tertiary amines of commercial origin contain small amounts of secondary amines as impurities. Thus, the appearance of a slight turbidity in the test is not to be taken as evidence for secondary amine.

Tertiary amines. Most of the aromatic tertiary amines respond to the following test: Dissolve the unknown in dilute. HCl and add 2ml of 2% $NaNO_2$ solution to this. A yellow or yellow green colour which turns dark greenish on making the solution alkaline indicates the aromatic tertiary amine.

Derivatives. (*i*) *Acetyl-derivative.* Place 1ml of the substance (or 1g of the powdered amine if solid) in a small flask fitted with a reflux condenser. To this add 5ml of an acetic anhydride acetic acid mixture (equal volumes) and reflux gently for 15-20 minutes. Pour the contents into water taken in a beaker, when solid anilide would separate out. Filter, wash with cold water and recrystallise from water or ethanol and note the melting point.

(*ii*) *Benzoyl-derivatives.* Place 1ml (or 1g) of the substance in a hard glass boiling-tube and add 20ml of 10% NaOH solution. Add 1-1.5ml of benzoyl chloride (0.5ml at a time) until, shaking the mixture vigorously in the securely corked boiling-tube, gives no further separation of the semi-solid benzoyl derivative. Shake the contents for another five minutes and finally filter off the solid, wash well with water, crystallise from alcohol, dry and determine the melting point.

$$\underset{\text{Benzoyl Chloride}}{C_6H_5COCl}+RNH_2\longrightarrow\underset{\text{Benzoyl derivative}}{C_6H_5CONHR}+HCl$$

(*iii*) *Picrate-derivatives.* Mix together about 0.5g (or 0.5ml) amine in 5ml alcohol and to this add 5ml of a cold saturated solution of picric acid in alcohol. Warm the mixture on a water-bath for 5-10 minutes. Cool, when picrate derivative would separate out. Filter, recrystallise it from benzene, dry and determine the melting point. Picrates are frequently employed as derivatives of the tertiary amines.

TABLE 10.7

Sl. No.	*Compound*	*Physical state*	*Nature*	*Melting point or Boiling Point °C*	*Derivatives*	*Melting point or Boiling Point °C*
1.	Ethylamine	Liquid	Aliphatic	B.Pt. 19	Benzoyl	71
2.	Diethylamine	,,	,,	56	Picrate	165
3.	Benzylamine	,,	Aromatic	185	Acetyl	60
					Benzoyl	105
4.	Aniline	,,	,,	183	Acetyl	114
					Benzoyl	163
5.	p-Toluidine	Solid	,,	M. Pt. 45	Acetyl	154
					Benzoyl	158
6.	α-Naphthylamine	,,	,,	50	Acetyl	160
					Benzoyl	161
7.	Diphenylamine	,,	,,	54	Acetyl	167
					Benzoyl	204
					Picrate	180
8.	β-Naphthylamine	,,	,,	113	Acetyl	134
					Benzoyl	162
9.	Dimethylamine	Liquid	Aliphatic	B.Pt. 193	Benzoyl	65
10.	O-Toluidine	Solid	Aromatic	M.Pt. 200	Acetyl	112
					Benzoyl	143
11.	Triethylamine	Liquid	Aliphatic	B. Pt. 90	Pircate	173
12.	Pyridine	,,	Aromatic	B. Pt. 116	Picrate	167
13.	Methylaniline	,,	,,	192	Acetyl	103
					Benzoyl	63
					Picrate	145
14.	Quinoline	,,	,,	238	Picrate	203

(b) Tests for amide group, $(-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2)$.

(*i*) Reaction with NaOH solution. Take 0.2g of the unknown in a boiling-tube and add 2ml of 10% NaOH solution. Boil the contents. Evolution of ammonia, which gives dense white fumes with a glass rod dipped in conc. HCl, indicates the presence of an amide group.

$$RCONH_2 + NaOH \xrightarrow{heat} RCOO^-Na^+ + NH_3$$

$$NH_3 + \underset{\text{Conc.}}{HCl} \dashrightarrow \underset{\text{(dense white fumes)}}{NH_4Cl}$$

(*ii*) *Hydroxamic acid test.* In a boiling-tube take 0.1g of the unknown with 2ml of IN-hydroxylamine hydrochloride and 2ml of IN-KOH solution. Boil the mixture for five minutes, cool and add 2-3 drops of ferric chloride. A red colouration is observed due to the formation of ferric hydroxamate.

Note. Nitriles also respond to this test.

TABLE 10.8

Sl. No.	*Compound*	*Physical state*	*Nature*	*Melting point or boiling point °C*	*Derivatives*	*Melting point or boiling point °C*
1.	Formamide	Liquid	Aliphatic	B.pt. 105	Xanthylamide	184
2.	Acetamide	Solid	,,	M.pt. 82	Picrate	107
3.	Oxamide	,,	,,	418	Oxanilide	245
4.	Urea	,,	,,	132	Urea nitrate	163
					Urea Oxalate	171
5.	Benzamide	,,	Aromatic	129	Benzanilide	162
					Benzoic acid	121

SPECIFIC REACTIONS

Acetamide, CH_3CONH_2.

Colourless deliquescent crystals readily soluble in water and alcohol.

(*i*) To 2ml of the aqueous solution add an equal volume of $FeCl_3$ solution. Production of wine-red colour which on heating gives reddish brown precipitate confirms acetamide.

(*ii*) On heating the substance with conc. H_2SO_4 a strong smell of vinegar due to the formation of acetic acid, is observed.

Urea, NH_2CONH_2.

Colourless crystalline solid, soluble in water and alcohol.

(*i*) *Biuret Test.* Heat 0.1g of substance in a dry test-tube a sublimate of biuret with the evolution of NH_3 is formed on the sides of the test-tube. Dissolve this in 2ml of distilled water, add a drop of very dilute $CuSO_4$ solution and 2ml of NaOH solution. Formation of a violet colour confirms urea.

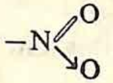
(*ii*) *Urea nitrate.* To 0.5g of urea add 3-5 drops of conc. HNO_3 and boil. Cool, white crystals of urea nitrate are obtained, M.pt. 163°C.

Benzamide. $C_6H_5CONH_2$.

White crystalline solid, soluble in hot water and alcohol.

(*i*) Heat 0.1g of the compound with 1ml of NaOH solution, ammonia is evolved.

(*ii*) Boil a little substance with dilute NaOH for five minutes, cool and acidify with dil. HCl. A white precipitate of benzoic acid is obtained, M.Pt., 121°C.



$-N\begin{matrix}/\!\!/ O\\ \searrow O\end{matrix}$

(c) Tests for Nitro Group, $-N\begin{matrix}/\!\!/ O\\ \searrow O\end{matrix}$. Presence of a nitro group is usually indicated by reduction or oxidation reactions.

(*i*) *Tollens' reagent test*. Dissolve about 0.5g of the compound in 10ml of 50% ethanol, then add 0.5g of NH_4Cl and 0.5g of zinc dust. Mix the reagents by shaking, then heat the mixture to boiling. Cool the mixture, filter after five minutes and test it with Tollens' reagent. A grey or black ppt. of Ag indicates the presence of nitro group. This is because of the reduction of nitro group to hydroxyl amine, or hydrazine, or an aminophenol, all these groups are oxidised by Tollens' reagent, which in turn, is reduced and gives a silver mirror.

$$C_6H_5NO_2 \xrightarrow{\text{Redn.}} C_9H_5NHOH + H_2O$$

$$C_6H_5NHOH + Ag(NH_3)_2^+ + OH^- \longrightarrow \underset{\text{(Silver mirror)}}{Ag} + C_6H_5NO + H_2O + 2NH_3$$

(*ii*) *Ferrous hydroxide test*. Mix 0.1g of the unknown with 5ml of freshly prepared 5% ferrous ammonium sulphate solution in a test tube. To this add 3-4 drops of 6N-H_2SO_4 followed by 2-3 ml of 2N-KOH solution in methanol. Cork the test-tube immediately and shake vigorously. Formation of a red-brown precipitate indicates presence of nitro group.

$$RNO_2 + \underset{\text{Blue-green}}{6Fe(OH)_2} \xrightarrow{4H_2O} RNH_2 + \underset{\text{Brown}}{6Fe(OH)_3}$$

Derivatives. Reduce these to primary amines and prepare solid derivatives of amines (see p. 204).

SPECIAL REACTIONS

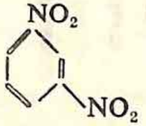
Nitrobenzene, $C_6H_5NO_2$.

Pale yellow liquid, insoluble in and heavier than water having characteristic odour of bitter almonds. B.pt. 211°C.

(*i*) On nitration with conc. HNO_3 and conc. H_2SO_4 yields *m*-dinitrobenzene, M.pt. 90°C.

(*ii*) To 1ml of nitrobenzene add a pinch of zinc dust and 2ml of conc. HCl and boil the mixture for five minutes. Nitrobenzene will be reduced to aniline, filter and with filtrate perform dye-test and carbylamine test as given in amines. Positive tests confirm nitrobenzene.

m-Dinitrobenzene,



Pale yellow crystalline solid insoluble in water but soluble in organic solvents, having M.pt. 90°C.

(*i*) Dissolve a few crystals in 2ml acetone and add a few drops of aqueous NaOH solution. A deep violet colouration is produced, and is turned red by acetic acid but distroyed by mineral acids.

(*ii*) Gives red brown colour on boiling with NaOH solution.

10.4 COMPOUNDS CONTAINING HALOGENS

The identity of these compounds is done on the basis of (*i*) Presence of halogen (Cl, Br or I)

(*ii*) Determining the melting or boiling point.

(*iii*) Preparing a suitable derivative.

To decide the aromatic or aliphatic nature, the compound is first hydrolysed with alcoholic KOH by boiling. The filtrate obtained is then tested with $AgNO_3$ solution. If the filtrate gives no precipitate or very light turbidity with $AgNO_3$ solution, the compound must be aromatic. In case a white or yellow precipitate is obtained the compound is either aliphatic or aromatic containing halogen in the side chain. A further confirmation is done by nitration. Only aromatic halogen compounds would undergo nitration.

Note: The ignition test in case of halogen compounds is inconclusive as some of highly halogenated aliphatic compounds burn with sooty flame. To illustrate——$CHCl_3$, chloral hydrate etc.

Table 10.9 Lists some halogen compounds with important informations required for their identification.

SPECIAL REACTIONS

Methyl iodide and ethyle iodide.

(*i*) Both give yellow precipitate with alcoholic $AgNO_3$ in cold.

(*ii*) Give addition product with pyridine.

Chloroform, $CHCl_3$.

(*i*) Gives carbylamine test.

(*ii*) Dissolve about 0.2 g of resorcinol in 1 ml of 30% NaOH

TABLE 10.9

Sl. No.	*Compound*	*Physical state*	*Solubility in water*	*Melting point or Boiling-point°C*	*Derivatives*	*Melting Point of derivative °C*
1.	Methy iodide	Liquid	Insoluble and havier	B.Pt. 42	β-Naphthyl ether	70
2.	Ethyl bromide	,,	,,	38	,,	37
3.	Ethyl iodide	,,	,,	73	,,	37
4.	Chloroform	,,	,,	61	Chloretone	97
5.	Iodoform	Solid	,,	M.Pt. 119	—	—
6.	Carbon tetrachloride	Liquid	,,	B.Pt. 78	—	—
7.	Chlorobenzene	,,	,,	132	2,4-Dintro	52
8.	Bromobenzene	,,	,,	156	2,4-Dinitro	75
9.	Iodobenzene	,,	,,	188	p-nitro	174
10.	Benzyl Chloride	,,	,,	179	p-nitro	71
11.	O-Chloro toluene	,,	,,	159	O-Chlorobenzoic acid	140
12.	m-chlorotoluene	,,	,,	162	m-Chlorobenzoic acid	153
13.	p-chlorotoluene	,,	,,	162	p-Chlorobenzoic acid	162
14.	m-Dichlorobenzene	,,	,,	173	4,6—Dinitro	103
15.	Hexachloro benzene	Solid	,,	M.Pt. 229	Chloranil	290

solution, add 1 ml of chloroform and warm gently the equeous layer turns red and shows a slight fluorescence.

Note. β-naphthol in place of resorcinol gives deep-blue colour, in aqueous layer, which fades to green.

(*iii*) Chloroform reduces Fehling's solution.

Iodoform, CHI_3.

(*i*) On heating, iodoform gives off copious violet vapours of iodine.

(*ii*) To a small amount of substance add 1g resorcinol and 2 ml alcoholic NaOH solution and heat. A red colour changing to violet is produced.

Carbontetra chloride, CCl_4.

(*i*) Gives isocyanide reaction.(*See p.*203)

(*ii*) Does not give a colouration with alkaline solutions of resorcinol or 1-or 2-naphthol (difference from chloroform).

Benzyl chloride, $C_6H_5CH_2Cl$.

(*i*) On oxidation with $K_2Cr_2O_7$ and conc. H_2SO_4 yields benzoic acid M. Pt. 121°C.

(*ii*) With quinoline yields addition products.

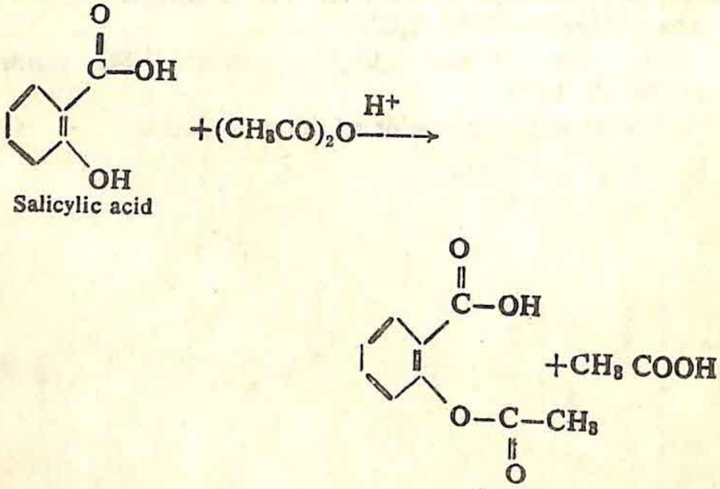
11

Organic Preparations

11.1. ASPIRIN (ACETYLSALICYLIC ACID)

Chemicals required. 1. Salicylic acid=5g,
2. Acetic anhydride=10ml,
3. Conc. H_2SO_4 =1–2ml.

Reactions.



Procedure. Into a 200ml conical flask introduce in the order named 5g of salicylic acid, 10ml of acetic anhydride, and 1-2ml of concentrated sulphuric acid. Shake the contents thoroughly and note the rise in temperature to 70°-80°C with accompanying solution of all the salicylic acid. The temperature of the solution remains above 70°C for several minutes because of the continuing exothermic reaction. Maintain the temperature 60°C-70°C for about 15 minutes by keeping the flask on a water-bath. Cool and then pour it in 100ml cold water taken in a 500ml beaker with stirring. Filter the precipitated crude product in a Buchner funnel using suction. Wash it with cold water, press the product on the filter to remove as much water, as possible, and then spread on a disk of filter paper to dry in the air recrystallize the crude sample of aspirin from benzene or ethanol to obtain colourless crystals. Hot water should not be used as a recrystallizing solvent, because aspirin undergoes partial hydrolysis to salicylic and acetic acids in the hot solution.

Yield. 4g.

Melting point. 135°C.

11.2. CAFFEINE (1,3,7—TRIMETHYLXANTHINE)

Caffeine is an alkaloid present in tea-leaves to the extent of 5 per cent. Hence, this is extracted from tea-leaves.

Chemicals required. 1. Tea leaves =50g,

2. Basic lead acetate =150ml (10% solution)
3. Dilute H_2SO_4,
4. Chloroform =75ml,
5. Decolourising carbon =0.5g.

Procedure. Boil 50g dry tea leaves in a 1 liter beaker with 500ml water for 20-25 minutes. Filter it through a muslin cloth into another beaker placed over a burner so that the filtrate is kept hot. To the clear filtrate add with constant stirring 150ml of 10 per cent solution of basic lead acetate (basic lead acetate solution is prepared by boiling lead acetate solution with excess of litharge). This precipitates tannins (naturally occurring polyphenols). Filter the hot solution and wash the residue with water. The filtrate is now treated with dilute sulphuric acid to precipitate lead sulphate which is further eliminated by simple filteration. The filtrate is now concentrated by evaporation and in the presence of decolourising carbon to about 150-200ml. Filter and shake with about 25ml chloroform in a separating funnel and separate the chloroform layer. Extraction is repeated thrice with 25ml portions of chloroform each time. Combine the chloroform extracts and remove most of the chloroform by distillation. The residue is then dissolved in small amount of hot water and the solution is concentrated by slow evaporation. Caffeine would start separating as long silky needles. Product so obtained is caffeine monohydrate which loses water molecule on heating to 100°C.

Yield. 0.5g.

Melting point. 235°C.

11.3 IODOFORM (TRI–IODOMETHANE)

Chemicals required. 1. Acetone = 2.5ml,
2. Potassium iodide solution (10%) = 100ml,
3. Sodium hydroxide solution (10%) = 40ml,
4. Sodium hypochlorite solution (5%) = 100ml.

Reactions.

$$NaOCl + H_2O + 2KI \longrightarrow NaOH + KOH + I_2 + KCl$$

$$CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CH_3COONa + 3NaI + 3H_2O$$

Procedure. Place 2.5ml of acetone, 100ml of 10 per cent aqueous potassium iodide solution and 40ml of 10 per cent aqueous sodium hydroxide solution in a 250ml conical flask. To this add slowly 100ml of 5 per cent sodium hypochlorite sloution with continuous stirring when the yellow iodoform will begin to separate almost immediately. Continue addition of sodium hypochlorite till the precipitate of iodoform separates. Allow the mixture to stand at room temperature for 10 minutes, and then filter at the pump, wash with cold water, and drain thoroughly. Place the crude material in a 50ml round-bottomed flask fitted with a reflux water-condenser add a small quantity of methylated spirit and heat to boiling on a water-bath. Dissolve the iodoform completely by adding more methylated spirit if needed. Filter the hot solution through a fluted filter-paper directly into a small beaker or conical flask and then cool in ice-water. The iodoform crystallises rapidly. Filter, drain thoroughly and dry.

Yield. 4.5g.

Melting point. 119°C.

11.4. MUCIC ACID, HOOC(CHOH)$_4$COOH

Chemicals required. 1. Lactose = 10g,
2. Nitric acid (Sp.gr. 1.15) = 100ml.

Reaction.

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} \xrightarrow[\text{Oxid.}]{HNO_3} \underset{\text{Mucic acid}}{HOOC\,(CHOH)_4COOH}$$

Procedure. Dissolve 10g of lactose in 100ml of nitric acid in an evaporating dish. Evaporate the contents in a fume cupboard until the volume has been reduced to about 20ml. The mixture becomes thick and pasty owing to the separation of mucic acid. Cool and dilute to 50ml with distilled water. Filter the contents on a Buchner funnel with suction and wash the crude acid with cold water. Recrystallise the crude product by dissolving it in the minimum volume of dilute sodium hydroxide solution and then adding dilute hydrochloric acid. During the reprecipitation with dilute HCl the temperature of the contents should not allow to rise above 25°C. Filter it and dry in an oven at 100°C.

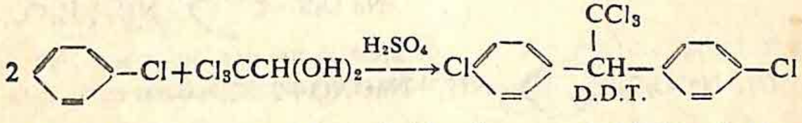
Yield. 5g (for better yield take galactose as starting material).

Melting point. 213°C (with decomposition).

11.5 D.D.T. (p,p'-DICHLORODIPHENYL-TRICHLOROETHANE)

Chemicals required. 1. Chlorobenzene=12ml,
2. Chloral hydrate=8.5g,
3. Conc. H_2SO_4=90ml,
4. Sodium carbonate solution (2%)=25ml,
5. Ethyl alcohol=50ml.

Reaction.



Procedure. Introduce 12ml of chlorobenzene and 8.5g of chloral hydrate crystals into a 250ml pyrex glass-stoppered reagent bottle. Dissolve all the crystals by warming it on a water-bath and with occasional shaking. Add slowly, 90ml of concentrated sulphuric acid after cooling the reaction mixture to room temperature. Put the glass stopper tightly by copper wire round the neck of bottle and shake mechanically for 1.5 hours. After allowing it to stand for fifteen minutes, pour the contents of the bottle slowly and with constant stirring into 400ml of water taken in a litre beaker. Crude D.D.T. separates out, which is filtered through a sintered glass funnel. Wash it several times with cold water. The solid obtained is now treated with 25ml of 2 per cent sodium carbonate for 5-10 minutes in a beaker. Filter and wash with distilled water until the filtrate is neutral to litmus, drain well with the help of an inverted glass stopper. Transfer the residue to a small mortar, add 50ml of ethyl alcohol and titurate with a pestle for 5-10 minutes. Filter it in a Buchner funnel using suction, wash twice with 25ml portions of ethanol, and continue the suction until most of the solvent has been drained off. Dry the residue at 70°C in a steam oven or on a water-bath.

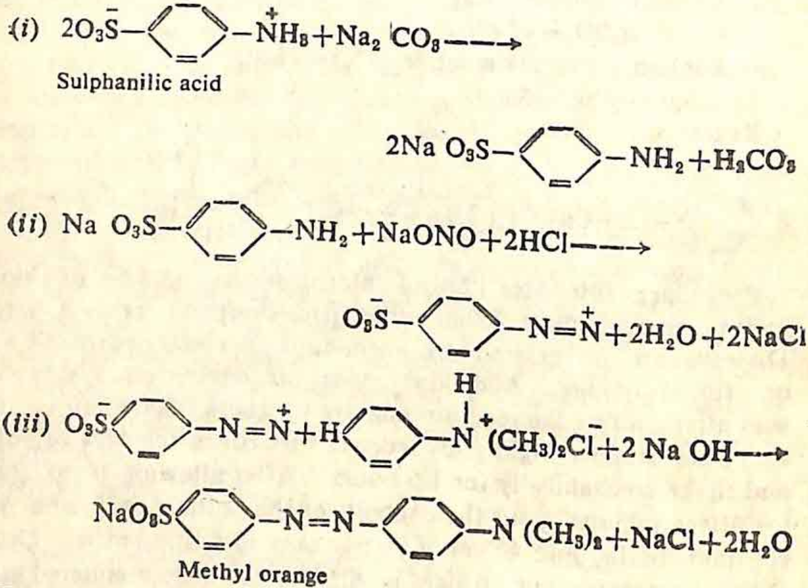
Yield= 7.5g.

Melting point. 108°C.

11.6. METHYL ORANGE

Chemicals required. 1. Sulphanilic acid=5g,
2. Dimethyl aniline=3ml,
3. Conc. HCl=6ml,
4. Glacial acetic acid=2ml,
5. Sodium carbonate=2g,
6. Sodium nitrite=2g,
7. Sodium chloride=5g,
8. Sodium hydroxide solution (20%)=20ml.

Reactions.



Procedure.

Step 1. Diazotization. Dissolve 5g of sulphanilic acid and 2g of sodium carbonate in 100ml beaker. Cool the solution to 0°C by adding ice into the beaker. To this add slowly and with stirring a well cooled solution of 2g sodium nitrite in 10ml water. A solution of 4ml of concentrated hydrochloric acid in 25ml of cold. water is then slowly introduced. Allow the reaction mixture to stand for about 15 minutes. Test for the presence of the nitrous acid by starch-iodide paper and if a deep blue colour develops on the paper by a drop of reaction mixture, destroy excess of nitrous acid by adding some solid urea. Crystals of diazobenzene sulphonate usually separate on cooling.

Step 2. Coupling.

Dissolve 3ml of dimethylaniline in 2ml of glacial acetic acid diluted with 15ml of water. Cool this solution with ice and pour it into the diazotized sulphanilic acid with continuous stirring. This process known as "coupling" is used for the preparation of all "azo" dyes. Allow the reaction mixture to stand for 10 minutes when crystals of methyl orange start separating. Complete the coupling process and, at the same time, convert the dye into its yellow sodium salt by the addition of approximately 20ml of 20 per cent solution of sodium hydroxide. The solution at this stage is faintly basic to litmus paper. Add 5g of pure NaCl, heat the contents of the beaker nearly to the boiling point on a water-bath and set the solution aside to cool. The dye separates in orange coloured crystals which are collected on a Buchner funnel with suction. Drain by pressing with a glass stopper and wash with a little ethanol and dry in an oven at 100°C.

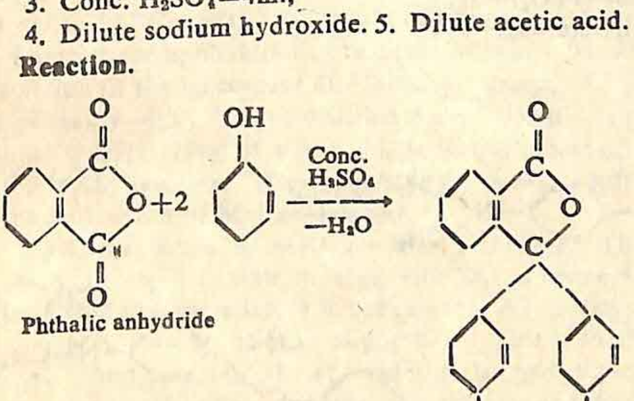
Yield. 8-9g.

Melting point. Do not attempt to take the melting point of the dye, since the dye decomposes before it melts.

11.7. PHENOLPHTHALEIN

Chemicals required. 1. Phenol=12.5g,
2. Phthalic anhydride=6g,
3. Conc. H_2SO_4=4ml,
4. Dilute sodium hydroxide. 5. Dilute acetic acid.

Reaction.



Phthalic anhydride

Phenolphthalein

Procedure. In a 250ml round-bottomed flask mix pure phenol, 12.5g with 6g of phthalic anhydride. Add 4ml of conc. H_2SO_4 and heat the flask in an oil bath at 115-120°C for about 9 hours until the mass becomes semi-solid and of a dark red colour. Then, pour the reaction mixture whilst still hot into 500ml of hot water taken in a one litre beaker, and boil until the odour of phenol has disappeared. Cool and filter the yellow, granular precipitate at the pump and wash it with water. Dissolve the solid in dilute sodium hydroxide solution, filter from the undissolved residue. Acidfy the filtrate with dilute acetic acid and a few drops of dilute hydrochloric acid with stirring, and allow to stand overnight. Filter the light-yellow granular crystals and dissolve in minimum amount of alcohol. Reflux the solution with 2g of animal charcoal for one hour on a water-bath. Filter the hot solution through a preheated Buchner funnel and evaporate the filtrate on a water-bath. The turbidity disappears and the phenolphthalein separates out in the form of a white powder. Filter this off and dry.

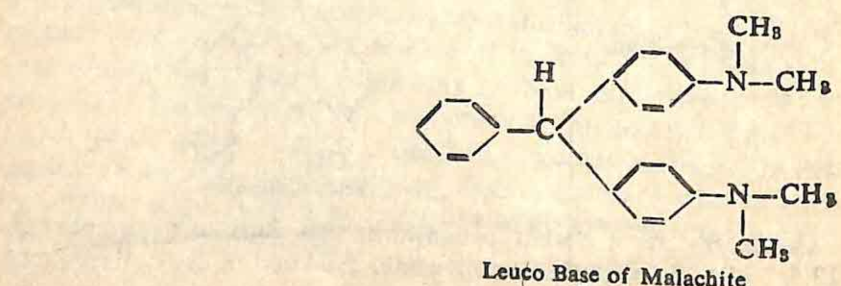
Yield. 4-5g.

Melting point. 256-258°C.

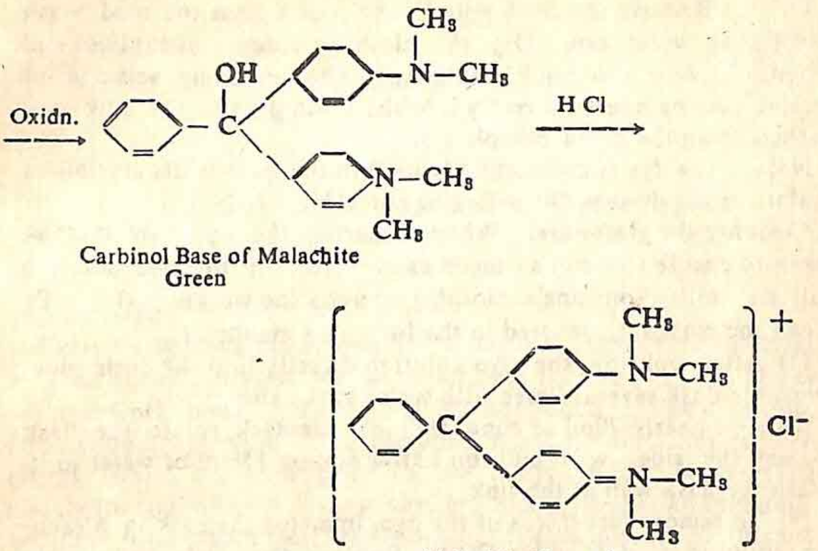
11.8. MALACHITE GREEN

Chemicals required. 1. Benzaldehyde=4ml,
2. Dimethyl aniline=4ml,
3. Fused zinc chloride (Powdered)=3g,
4. Conc. HCl.=3ml,
5. Lead dioxide (PbO_2)=3g,
6. Sodium sulphate=3g.

Reactions.



Leuco Base of Malachite Green.



Carbinol Base of Malachite Green

Malachite Green A (Salt)

Procedure.

Step 1. Preparation of leuco base. Place 4ml each of benzaldehyde and dimethylaniline along with 3g of coarsely powdered fused zinc chloride into a 500ml distilling flask. Lower a thermometer into the flask and warm it on small semiluminous flame of Bunsen burner to 130°C-140°C. Maintain this temperature for ten minutes by intermittent application or removal of heat. This results in the formation of the leuco-base of Malachite green. Cool and dilute the contents with 150ml of distilled water. Distill the contents to collect at least 125ml of water, this boils out excess of benzaldehyde and dimethyl-aniline. A gummy blue-green mass left in the flask is the leuco-base of Malachite green.

Step 2. Oxidation of the leuco base to the dye. The leuco base obtained in step-1 is, now, treated with 3ml of concentrated hydrochloric acid and the mixture is shaken for 2-3 minutes to dissolve as much of the leuco-base as possible. This is further diluted by adding 150ml of water. After shaking it add 3g of lead dioxide (PbO_2), when immediate deepening of the colour takes place. Shake the flask for 2 minutes and precipitate out lead as lead sulphate by adding 3g of sodium sulphate.

Step 3. Dyeing the cloth. The above solution is now boiled for a few minutes and nearly 20ml of this is filtered into a 50ml beaker. Put woollen piece of cloth in the solution and boil for 2-3 minutes. Remove the cloth with the help of a glass rod and wash directly at water tap. Dry the cloth in absence of sunlight and fasten it in your note-book with a tag. The remaining solution of the dye may be poured directly into the drain pipe in the sink and washed down the drain completely.

Note. The dye is commercially used in the form of its crystalline oxalate or the double salt with zinc chloride.

Cleaning the glassware. While preparing the dye care must be taken to ensure that not so much as one drop of the dye solution will be spilled on one's clothing or upon the working table. To clean the glassware proceed in the following manner:

(1) After pouring the dye solution directly into the drain pipe, wash the flask several times with water at the sink.

(2) Add nearly 20ml of conc. HCl into the flask, rotate the flask to wet the sides well and boil after adding 150ml of water to it. Wash the flask well at the sink.

(3) To remove last traces of the dye, immerce the flask in bleaching solution ($CaOCl_2+Na_2CO_3$). Remove the flask with the old pair of tongs after 5-10 minutes and wash well with water at the sink.

(4) The beaker, funnel and other glassware are also washed in a similar way.

(5) Any spot of dye on the skin may be removed by applying a little bleaching solution and allowing it to remain 1-2 minutes and then washing with water. The smell of chlorine can be easily removed by an alcohol rub.

12

Food Adulteration and its Detection

Introduction

Every living being needs food for its survival. Plants need sufficient amount of soil nutrients, air, water and sun light to live. In our day to day work body performs many vital functions like digestion, circulation, respiration and excretion. All these activities require energy, which the food gives to the body. Food is required mainly for building the body muscles, blood, bones and tissues. Besides, food also repairs the worn out tissues and cell. Different types of foods play different role in keeping the body fit. Unfortunately number of food stuffs in the market are adulterated and 30-40 percent of edibles sold in the market are adulterated. These adulterated food stuffs are responsible for large number of diseases and thus are disastrous to human health.

Now the question arises, what is food adulteration?

The general feeling is that the intentional addition of non-permitted foreign matter to food or the removal of useful ingradients from food is adulteration. This involves the wilful act on the part of the adulterator. According to the prevention of Food-Adulteration Act of 1954 food adulteration includes the intentional addition or abstraction of those substances which adversely affect the quality of foods as well as their incidental contamination during their periods of growth, processing, transportation and distribution.

The safe limits for different adulterants have been suggested by the International Codex Alimentarius Commission. It is a collection of internationally adopted food standards. It also includes the provisions in respect of food hygiene, food addifives, posticide residues, contaminants, labelling and presentation, methods of analysis and sampling.

A number of existing food standards in India are also based on the international codex alimentarius. There are two national standard of quality at present (*a*) The PFA (Prevention of Food Adulteration) standards these prescribe the minimum requirements for all types and categories of food. The rules were first introduced in 1955 and have been amended from time to time.

(*b*) FPO (Fruit Products order) Standard were introduced in 1946. It lays down minimum standards relating to the quality of various fruits and vegetable products. It also prescribes the standards of hygiene in the factories and the packing and labelling materials employed in the factories.

The adulterated food has a direct and immediate impact on public health and it is more pronounced in the poor and undernourished population. The various adulterants which may be present in some of the food-stuff have been given in Table 12.1.

TABLE 12.1

Food type	*Food stuffs*	*Adulterants*
Vegetable oils and fats	Vanaspati	Animal body fat, prohibited colour, rancid fat, deficiency of sesame oil.
	Vegetable oils	Rancid oils, tea sead oil, oil soluble dyes, argemone oil, mineral oil.
Milk and Milk products	Milk	Coaltardyes, water, fat deficiency, antibiotics, and starch.
	Khoya, Channa and condensed milk, Butter, Ghee	Starch and fat deficiency, paper and excess moisture. Prohibited colour, artificial sweeteners and deficiency in milk fat.
Cereals	Wheat	Stones, mud, sand and insect infestation.
	Atta, Suji and maida	Excess bran, talc, foreign starch, sand and chalk powder.
Pulses	Chana dal, arhar dal and moong washed, Besan	Kesari dal coloured with coal-tar dye or polished with talc. Maize and peas flour, Kesari pulse and coal tar dye.
Sweetening agents	Sugar	Dirt, sūji, fine white sand and corn filings.
	Gur	Artificial colouring matter, sand & dirt.
	Bura (Sugar)	Talc, excess moisture, and atta.

Food Type	*Food stuffs*	*Adulterants*
	Honey	Cane sugar, commercial invert sugar and colouring matter.
Non-alcoholic Beverages	Soft drink	Prohibited colours, saccharin above the permissible limits, mineral acids, lead, arsenic and copper.
	Tea	Dust, foreign & exhausted leaves added colour, woody stalks, saw dust, black gram husk, cashew husk and tamarind seed powder.
	Coffee powder	Chicory without declaration, tamarind seeds, roasted dates husk powder and exhausted coffee.
Alcoholic Beverages	Alcoholic Beverages	Methanol, excess water fuel oil.
Confectionary	Sweatmeats	Harmful colours, flavours, rancid stuff, talc, vegetable oil in place of ghee.
Miscellaneous	Supari	Foreign seeds or nuts, stones, colour white stone, sand.
	Common salt	Excessive salts and grit.
	Ground nuts	Fungal contamination, shrivelled nuts. Grit,
	Biscuits	Talc and other foreign matter.

The amount of foreign matter in cereals and pulses can be determined by hand picking method. Weigh 5g of the sample on a glaze paper. Pick up all foreign matter by hand or using forceps. Weigh the total foreign matter and calculate its percentage. Kesari Dal can also be detected and estimated in a similar manner. All the grains of kesari dal are triangular in shape and dirty grey in colour with dark spots on the surface. Starch in milk butter khoya or other food stuffs can be defected by adding 4-5 drops of iodine to a suspension of butter or any other food stuff. Boil and cool the solution. Formation of a blue colour or precipitate indicates the presence of starch.

Excercise 12.1. *To detect the adulteration of vanaspati ghee in pure ghee.*

Principle. The presence of vanaspati ghee in pure ghee can be detected by testing for seasame oil which is present in vanaspati ghee. The test is known as Bodoudoiun test.

Procedure. Take 10ml of melted ghee in a test tube. In another test tube dissolve 0.2gm of sucrose in 10ml of dil HCl. Mix the two solutions and shake thoroughly. Heat the mixture until it becomes colourless and keep the solution for 10 minutes. Formation of pink or red colour indicates the presence of vegetable ghee.

Result. The given sample of pure ghee contains/does not contain Vanaspati ghee.

Exercise 12.2. *To detect the adulteration of invert-sugar in honey.*

Principle. Honey is the saccharine product gathered by bees from the nector of flowers. The colour of honey varies from almost colourless to nearly black depending upon the flowers from which the nector has been taken. The main constituents of honey are (*a*) dextrose, (*b*) fructose, (*c*) sucrose (*d*) dextrins, (*e*) mineral matter, (*f*) proteins and (*g*) wax. There should be no invert sugar present in the honey. During the manufacture of invert sugar by acid hydrolysis of sucrose, 5-hydroxymethylfurfuraldehyde (HMF) is also formed. The detection of invert sugar in honey therefore depends on the formation of red colour when HMF reacts with resorcinol. This is known as Fiehe's test modified by Lampitt, Hughes & Rooke.

Procedure. Dissolve 10g honey in 10ml of cold water. Shake it gently with 20ml of diethylether. Decant off the ether and evaporate it to dryness. Dissolve this residue in 10ml of ether.

(*a*) To 2ml of this extract add 2ml of a fresh 1% resorcinol in conc. HCl. Formation of a pink colour in the acid layer, which becomes cherry red at the junction of the layers indicates the presence of invert sugar.

(*b*) Evaporate the remaining ether extract in a porcelain dish at room temperature and to the residue add 2ml of fresh aniline acetate solution (Aniline acetate solution is obtained by mixing 1ml of aniline with 4ml of glacial acetic acid) keep this solution for 15 minutes. Appearance of a pink or orange colour confirms the presence of invert sugar.

Result. The given sample of honey contains/does not contain invert sugar.

Exercise 12.3. *To detect the adulteration of tea seed oil in the given sample of vegetable oil.*

Principle. The detection of tea seed oil in vegetable oil is based on the formation of deep green colour by reflected and transmitted light in Fitelson's test for tea seed oil.

Procedure. Mix together 0.8ml of acetic anhydride, 1.5ml of chloroform and 0.2ml of conc. H_2SO_4 in a test tube. Cool it in an ice bath for 1 or 2 minutes and add 6-7 drops of the given oil. If the liquid appears cloudly make it clear by adding dropwise acetic anhydride. Keep the test tube in an ice bath for 5 minutes, development of a green colour in the reflected and transmitted light indicates the presence of tea seed oil. Add 10ml of dry ether and mix the contents by shaking the tube. Brown colour is formed which changes to red within 1 minute and finally fades. This test confirms the presence of tea seed oil in the given sample of the vegetable oil.

Result. The given sample of vegetable contains/does not contain tea seed oil.

Exercise 12.4. *To detect the adulteration of coal tar dyes present in food stuffs.*

Principle. The non-permitted colours in the food-stuff act as adulterants. Though the addition of colour given good shape to the finished food, it is advisable, however, to limit the use of even these permitted colours. No dye can be said to be absolutely safe. The dyes considered safe today may prove toxic in future. We shall be interested in the detection of water-soluble acidic dyes. These can be detected by boiling the food extract with wool.

Procedure. Grind 5g of the sample thoroughly with 25ml of 2% ammonia and 70% alcohol. Allow it to stand for about 2 hours. Filter and evaporate the filtered liquid on a water bath to dryness. Dissolve the residue in 15ml of water containing acetic acid (3-4ml of acetic acid).

Take a 20cm strip of wool, boil it first in dilute sodium hydrooxide solution and then in water. Add this strip to about 20ml of the above prepared solution. Boil it for 10-15 minutes. Wash the wool with tap water and transfer it a 100 ml beaker and boil gently with 20ml of dilute ammoina. If the solution becomes coloured it indicates the presence of a coaltar dye in the food stuff.

Result. The given sample of food stuff contains/does not contain the coal-tar dye.

Exercise 12.5. *To detect the adulteration of Rhodamine B colour in chilly powder.*

Principle. Red chillies are contaminated with powdered bran, geru, foreign starch and rhodamine B. Rhodamine B is used to colour them red artificially. It is carcinogenic and may cause pathological lesions in vital organs liken kidney, spleen and liver.

Procedure. Extract the red colour in ether or alcohol. To 5ml of this extract add 5ml of conc. HCl. Formation of dark pink colour, confirms the presence of Rhodamine B. The light pink colour may be treated as negative.

Result. The given sample of chilly powder, contains/does not contain Rhodamine B.

Exercise 12.6. *To detect the adulteration of lead chromate in whole turmeric.*

Principle. Whole turmeric is polished with lead chromate or metanil yellow. The adulteration of lead chromate may cause anaemia, abortion, paralysis, mental retardation, accumulation of lead in the body and blood. It may also cause brain damage in children.

Procedure. Ash about 2.0g of the sample and dissolve it in 10ml of (1:7) H_2SO_4. Boil it for five minutes and filter. To 5ml of the filtrate add about 0.5ml of 2% diphenylcarbazide in alcohol. Formation of dark pink colour confirms the adulteration of lead chromate.

Result. The given sample of whole turmeric, contains/does not contain the adulteration of lead chromate.

13

Determination of Molecular Weights

Dalton suggested that the relative weights of atoms could be determined if only the ratios of the number of atoms of each element in a compound is known. Avogadro suggested that *equal volumes of all gases under similar conditions of temperature and pressure, contain the same number of molecules.* The atomic weight expressed in grams is known as gram-atom. The molecular weight expressed in grams is called gram-molecule. The gram-molecular volume of an ideal gas according to Avogadro's hypothesis is taken to be 22.4 litres at N.T.P. The latest experimental value for Avogadro's number is $6.02252\ (\pm 0.00028) \times 10^{23}$, however for most simple calculations this value is 6.0×10^{23}. Hence we can define a gram-atom of an element as the mass in grams, of the Avogadro number of atoms of the element concerned.

The molecular weight of a volatile substance can be determined by Victor Meyer's method and that of a non-volatile solute can be determined using Rast's method.

Exercise 13.1. *To determine the molecular weight of benzene by Victor Meyer's method.*

Theoretical principle. Vapour density of a gas or vapour is defined as the number of times a certain volume of it, is heavier than the weight of an equal volume of hydrogen at the same temperature and pressure. A known weight of a volatile material is made to vapourise and the volume of air displaced is collected and measured. The molecular weight can be calculated as follows:

Molecular weight, $M = 2 \times$ Vapour density, (v.d.)

Materials required. Victor Meyer tube, benzene, rubber tube, rubber cork, tripod stand, graduated gas cylinders.

Procedure. Clean and dry the Victor Meyer's tube, and place a pad of glass wool with the help of glass rod. Fill in about 300ml of water in the outer jacket. Set up an assembly as shown in Fig. 13.1 on a tripod stand Stopper the Victor Meyer tube loosely with

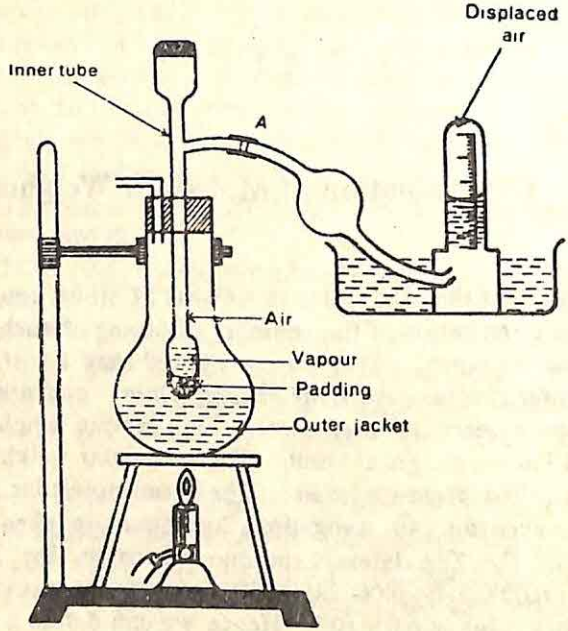


FIG. 13.1

its rubber cork. Weigh 0.1-0.2g of liquid, accurately in a pre-weighed tube. The tube is sealed and a jet is drawn. Heat the Victor Meyer tube till no more air is there in the vessel. Keep the gas cylinder completely filled with water. Cut the capillary end quickly and drop it in the Victor Meyer tube by removing the cork. The liquid vapourises and the water in the gas cylinder will be displaced. If it appears that the displaced air will be more than the capacity of gas cylinder, replace this by the second tube. Wait for about 5 minutes after the last bubble of the displaced air has been collected. Read the volume of the displaced air by equalising the water level inside and outside the tube. Record the temperature of the water in the tall cylinder (See Fig 13.2) and the barometric pressure. Repeat three sets of observations.

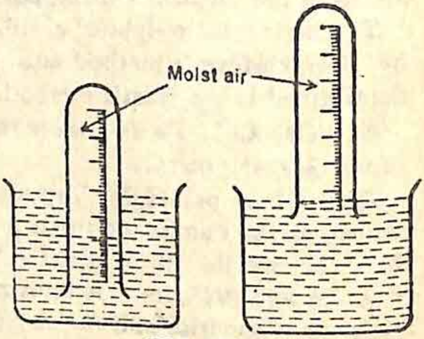


FIG. 13.2

Observations and calculation.

Weight of the tube= W_1 g
Weight of the tube-liquid= W_2 g
Weight of the liquid taken= W_2-W_1 g
The volume of air displaced= v ml
Barometric pressure= P
Temperature of water in the cylinder= t°C.
Aqueous tension at t°C= a, mm Hg
Relative humidity of air= h%
Corrected pressure of displaced air:

$$p=P-a\left(1-\frac{h}{100}\right)=p \text{ mm Hg}$$

The molecular weight of the given liquid;

$$M=RT\,\frac{(W_2-W_1)}{pv} \qquad \ldots (13.1)$$

Result. The molecular weight of the given liquid was found to be ....

Exercise 13.2. *To determine the molecular weight of naphthalene by Rast's Method.*

Principle. The basis of Rast's method of determining molecular weights is the use of camphor as a solvent. This is because, camphor, has a high value for freezing point depression constant K_f, i.e., 40°C for 1 mole of solute in 1000g of solvent. Thus a 10 per cent solution of solute in camphor will have a m.pt. several degrees lower than that of pure camphor and the depression can be measured fairly accurately with an ordinary thermometer. Camphor is a good solvent for most of the substances. Rast method can be used for those solutes which are soluble in comphor and do not react chemically or decompose when heated to the melting point of camphor. The advantages of Rast's method are that it is quick, needs no special apparatus, and requires only a small amount of material.

Materials required. A one-tenth degree thermometer, naphthalene, camphor, liquid paraffin bath, capillary tube.

Procedure. Take a pre-weighed dry test tube. Pour into it about 10 mg of naphthalene and 100 mg of camphor and weigh the test tube. Seal the open end of the tube by drawing a capillary. Heat the contents of the test tube slowly to about 180°C. Keep on rotating the tube to allow a proper mixing of the two components. Cool the tube quickly in a water bath. This is done to avoid the loss of camphor due to sublimation. Break open the test tube, take out the solid mass, powder it finely. Fill this powder in a melting point capillary and take its melting point when the last crystals have just melted. (See Fig 13.3). Repeat this observation at least three times and take the average of these temperatures as t_1°C. Now take pure camphor, powder and fill it up in the melting point capillary and determine its melting point, take three readings and t_2°C be the average of these temperatures.

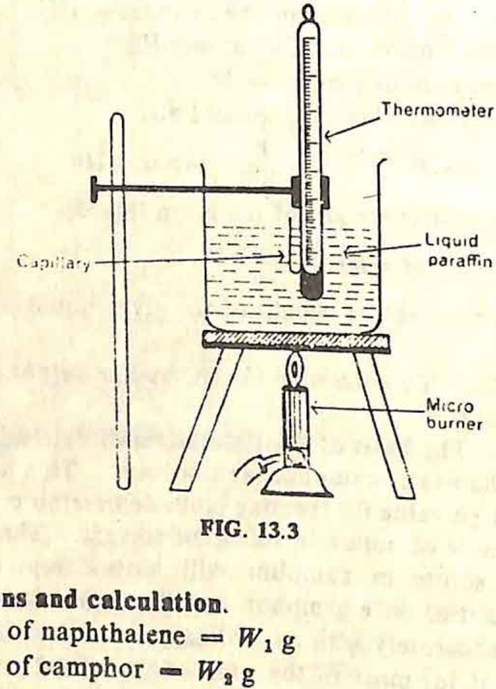


FIG. 13.3

Observations and calculation.

Weight of naphthalene = W_1 g

Weight of camphor = W_2 g

Average melting point of the mixture = t_1°C

Average melting point pure camphor = t_2°C

Depression in freezing point, $\Delta T_f = t_2 - t_1$

Molal depression constant for camphor = 37.7°C.

Since there is a depression in freezing point on addition of a non-volatile solute:

$$\therefore \quad \Delta T_f = \frac{K_f \times W_1 \times 1000}{M \times W_2} \qquad \ldots (13.2)$$

$$\text{or} \quad M = \frac{K_f \times W_1 \times 1000}{\Delta T_f \times W_2} \qquad \ldots (13.3)$$

On substituting the value of K_f, W_1, W_2 and ΔT_f, M the (molecular weight of naphthalene) can be determined.

Result. The molecular weight of naphthalene was found to be. . .

14

Surface Tension and Viscosity

Introduction

In a gas, the molecules are at random motion and the space between them is large, as compared to the size of the molecules. Since the molecules in a liquid are always relatively close together and these forces are of much greater significance than in the gas phase. However, it is much more difficult to systematise or to predict quantitatively the properties of liquids such as density, viscosity and vapour pressure, than it is to handle the correlation of gaseous properties.

One approximate description of the liquid phase postulates that in a liquid there are holes that, move about through the mostly continuous liquid somewhat as molecules fly about through the mostly empty gas phase. A hole in a liquid moves by virtue of being filled by molecular diffusion which in turn creates another hole adjacent to the original one. The liquid may thus be regarded somewhat like a gas "Turned inside out."

An alternative approach regards liquid as a slightly disordered solid. A particularly significant and perplaxing problem in liquid theory is how to describe the structure of water and how to account for its properties. Of numerous models that have been proposed, no one is completely successful. We shall learn to determine two important properties of liquids, i.e., surface tension and viscosity, in this Chapter.

14.1. SURFACE TENSION

A droplet of liquid such as a rain drop or a globule of mercury tends to assume a spherical shape. This is a manifestation of the general tendency of a liquid to reach a condition in which the surface area has the smallest possible value for a given volume of material. The molecules in the surface of a liquid are in different environment from molecules in the body of the liquid. It is attracted equally in all directions by other molecules surrounding it. Consequently, the net resultant force of attraction on the molecule in the liquid is zero. However, the molecule near the surface of the liquid is subjected to net downward forces of attraction as there are no molecules above it to attract. Thus these unbalanced attractive forces acting downwards tend the molecules at the surface of a liquid to be pulled into the body of the liquid. This inward attraction causes the surface to contract. The surface of the liquid therefore, behaves as if it were in a state of tension.

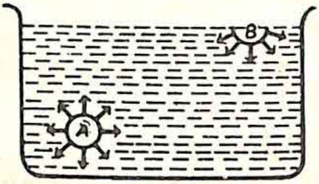


FIG. 14. 1. Forces on a molecule at the surface and interior of a liquid.

Imagine that a spherical droplet of a liquid is distorted to a flattened shape so that a longer area of surface is established. Work must be done in order to form a new surface, and this work is equal to the force exerted on the surface multiplied by the distance through which the force acts. If the force is applied perpendicularly to an imaginary line of length centimeter in the surface and pulls the line a distance x centimeter, a new area of magnitude lx is produced. The force required is γ_1, where γ_1 is surface tension and the distance through which this force moves is x, so that the work done $\gamma_1 x$. The work required per unit surface area is thus numerically equal to the surface energy per unit area of surface. Surface tension may also be defined as the work required to produce a unit increase in the surface area. In CGS units it is expressed as ergs cm^2 or dynes/cm, where as the SI units are Newton m^{-1}.

Measurement of surface tension. The commonly used method of measuring surface tension is the capillary rise method. Consider a fine capillary tube of uniform radius r placed in a liquid that wets the walls of the tube. Since the force of surface tension, γ acts along the inner circumference of the liquid. The liquid begins to rise and keeps on rising until upward force F_1, due to surface tension is balanced by the downward force F_2 due to the weight of the liquid. This is shown in Fig. 14.2.

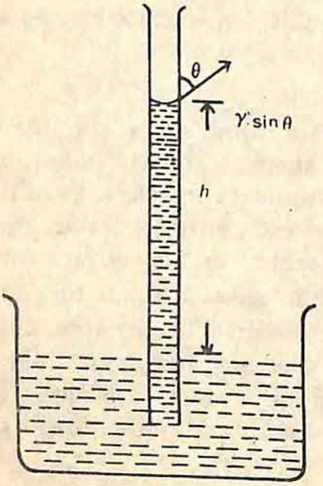


FIG. 14.2. Capillary rise methods for measuring surface tension.

Since the force due to surface tension is acting at an angle θ, known as contact angle.

$$F_1 = 2\pi r\, \gamma \cos\theta \qquad \ldots (14.1)$$

If the liquid rises a height h in the tube, above the level of the liquid outside, the downward force F_2 is given by

$$F_2=\pi r^2\ hdg \qquad \ldots (14.2)$$

where d is the density of the liquid and g is the acceleration due to gravity. At equilibrium,

$$F_1=F_2$$

$$2\pi r\ \gamma \cos\theta=\pi r^2\ hdg$$

$$\gamma=\frac{1}{2\cos\theta}\ r.\ hdg. \qquad \ldots (14.3)$$

for many liquids $\theta=0$; $\cos\theta=1$

$$\gamma=\tfrac{1}{2}r\ hdg \qquad \ldots (14.4)$$

The surface tension of a liquid may be determined using the above equation. For most accurate work corrections must be applied for (*i*) volume of the meniscus, (*ii*) density of the vapours collected above the liquid. Equation (14.4) modifies to

$$\gamma=\tfrac{1}{2}\left(h+\frac{r}{3}\right)(d_l-d_v)\ rg \qquad \ldots (14.5)$$

where d_l is the density of the liquid and d_v is the density of the vapours. The instrument employed for the purpose is known as the Stalagmometer and conists of a bubbled capillary tube as shown in Fig. 14.3.

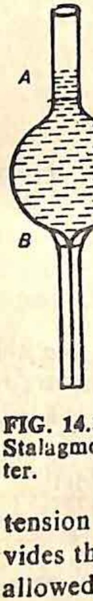


FIG. 14.3. Stalagmometer.

There are two types of methods that are employed for the measurement of surface tension, i.e., (*a*) drop weight method, (*b*) drop number method.

Drop weight method. This method is based on the fact, that the size of the drop falling off from the end of a capillary tube, depends on the surface tension of the liquid and the size of the capillary end, which provides the outerline of attachment for the drop. When a liquid is allowed to flow through a capillary tube, a drop will increase in size upto a certain point and then fall off. The drop will fall when its weight w (mg) just exceeds the surface tension force, acting along the circumference of the capillary, i.e.,

$$w=mg=2\pi r\ \gamma \qquad \ldots (14.6)$$

where w is the weight of the drop, m is its mass and $2\pi r$ is the external circumference of contact of the drop with the capillary tip. For two liquids 1 and 2 we can write:

$$w_1=m_1g=2\pi r\gamma_1$$

$$w_2=m_2g=2\pi r\gamma_2$$

$$\therefore\ \frac{w_1}{w_2}=\frac{\gamma_1}{\gamma_2} \qquad \ldots (14.7)$$

This method can be used for comparing the surface tensions of two different liquids. If γ_1 for any one of the two liquids is known, γ_2 can be calculated.

Drop number method. In this method, number of drops formed by equal volumes of two liquids are counted. Since with two different liquids, masses of equal volumes are proportional to their densities. If n_1 and n_2 are the number of drops produced from the same volume v of two liquids, then,

For liquid 1

Mass of one single drop, $m_1 = \frac{v}{n_1} \times d_1$

$$\therefore\ 2\pi r \gamma_1 = \frac{v}{n_1} d_1 \qquad \dots (14.8)$$

For liquid 2

Mass of one single drop, $m_2 = \frac{v}{n_2} d_2$

$$\therefore\ 2\pi r \gamma_2 = \frac{v}{n_2} d_2 \qquad \dots (14.9)$$

On dividing Eq. (14.8) by (14.9) we get,

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2 d_1}{n_1 d_2} \qquad \dots (14.10)$$

where γ_1 and γ_2 are the surface tensions, and d_1 and d_2 are the densities of the two liquids. One of the liquids, is, generally water as its surface tension data at different temperatures is available.

Exercise. 14.1. *To determine the surface tension of a liquid.*

Material required. Stalagmometer, pinch clamp, distilled water, rubber tube, organic liquid, specific gravity bottle.

Procedure. Attach a small piece of clean rubber tubing provided with a pinch clamp to the upper end of the stalagmometer. The purpose of the pinch clamp is, to control the rate of flow of liquid by limiting the influx of air. Clean the stalagmometer with chromic acid to remove the grease followed by washing with distilled water, and repeat this process several times.

Open the pinch clamp, immerse the dropping tip in the water, suck at the end of the rubber tube until the stalagmometer is filled above the mark. Close the clamp and adjust it in such a manner that 10-15 drops come out per minute. Count the number of drops as water flows from the mark *A* to *B*. Repeat sucking-in and running-out of water (See. Fig. 14.4).

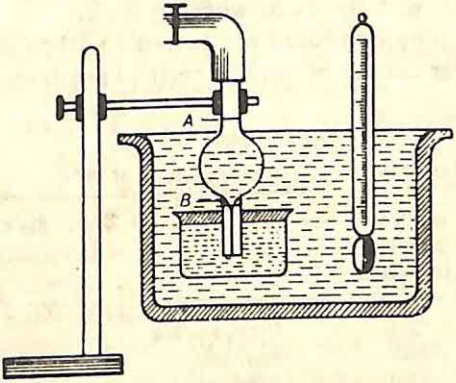


FIG. 14.4

Now suck the given liquid, by adjusting the clamp and count the number of drops when the meniscus passes the upper mark A and stop when it passes the lower mark B. Repeat the measurements, check that results should not differ by more than one per cent.

Determine the weight of empty specific gravity bottle w_1, filled with water (w_2) and filled with the given liquid, calculate d_1 and d_2. Note down the temperature of measurement and the surface tension of water is taken from the tables at this temperature.

Observations. Temperature of measurement= . . . °C

Surface tension of water, γ_1= dyne/cm

Density of water, d_1= g/c.c.

Density of liquid, d_2= g/c.c.

Sl. No.	*Number of drops*				*Surface tension of liquid,* γ_2 *dyne/cm.*
	n_2	n_2	n_1	n_1	
1.	...	...	...	...	...
2.	...	...	...	...	...
3.	...	...	...	...	...
4.	...	...	...	...	...
5.	...	...	...	...	...

Precautions. 1. The stalagmometer should be washed thoroughly to remove any grease in the capillary.

2. Care must be taken that the tip of the stalagmometer does not come in contact with hands or working table.

3. The rate of dropping should not exceed 15 drops per minute.

4. Stalagmometer should be held in vertical position.

TABLE 14.1

Surface tension for various liquids at 20°C

Liquid	*Surface tension (dyn/cm)*	*Liquid*	*Surface tension (dyn/cm)*
Water	72.7	Ethyl acetate	23.8
m-Cresol	37.5	Acetone	23.5
Benzene	28.9	Ethanol	22.5
Acetic acid	27.6	n-Hexane	18.4
Chloroform	27.2	Ethyl Ether	17.0
Carbon-tetrachloride	26.8	...	...

Exercise 14.2 – *To determine the concentration of an unknown solution of acetic acid – Water.*

Procedure.—Count the number of drops of pure acetic acid in the stalgmometer. Count the number of drops of water. Prepare three solutions as follows :

Solution A (15.0 ml acetic acid + 5.0 ml water), Solution B (10.0 ml acetic acid + 10.0 ml water) Solution C (5.0 ml acetic acid + 15.0 ml water). Count the number of drops in each case. Plot a graph between the number of drops against the percentage composition. For the lower concentration range straight line is obtained. Also count the number of drops of the given solution. From the plot calculate the concentration of the given solution.

14.2. VISCOSITY OF LIQUIDS

The molecules in a liquid are so closely packed that the liquids cannot be compressed to any appreciable extent. All liquids flow under an applied stress, which could even be the force of their own weight, the ease with which they flow differs from liquid to liquid. For example, glycerine and caster oil flow very much slower than water, benzene and petrol, the liquids which flow slow are said to be more viscous. The property of resistance to flow when a stress is applied to a liquid is called its viscosity. In the process of flow, the molecules comprising the fluid move past one another and viscosity arises from what can be termed the 'frictional' effects of relative motion. When a liquid is flowing through a circular tube the flow pattern is called streamline or viscous or laminar. The flowing fluid can be viewed as being composed of concentric cylindrical layers with all the molecules in any one layer moving with the same velocity, and with each molecule following a course parallel to the tube axis without lateral motion. Each successive layer from the wall inward toward the axis is found to be moving faster than the one outside it, so that the velocity increases to a maximum at the centre of the tube.

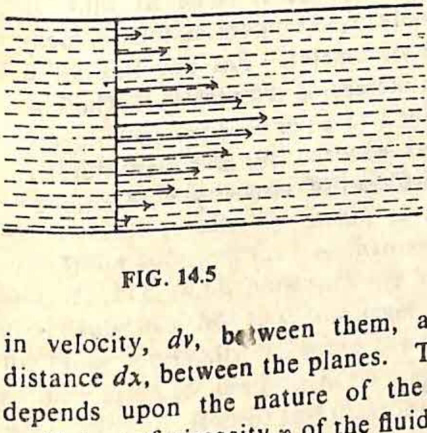


FIG. 14.5

Imagine two small planar surfaces, each of area A, located within a flowing fluid and paralleled to one another and to the axis of flow, each of the planes representing a surface of constant velocity (See Fig. 14.5). In order to maintain the velocity of the flow at one plane greater than that at the second by an amount dv, a force f must be exerted. The force is proportional to the area of the planes and to the difference in velocity, dv, between them, and inversely proportional to the distance dx, between the planes. The constant of proportionality depends upon the nature of the fluids and is designated as the coefficient of viscosity η of the fluid. These relations are expressed in the equation,

$$F = \eta A \frac{dv}{dx} \qquad \ldots (14.11)$$

For many liquids and almost all gases, the coefficient of viscosity is found to have a constant numerical value at a specified temperature. J.L.M. Poiseuille showed that the volume v of liquid of viscosity coefficent η, flowing through a tube in time t seconds is given by

$$\eta = \frac{\pi P r^4 t}{8 l v} \qquad \ldots (14.12)$$

where r is the radius of the tube, l is the length of the tube and P is the driving pressure. Since it is difficult to measure accurately the dimensions of the tube, therefore, one measures relative time of flow of various liquids in the same tube and compares it with water. Using Poiseuille's equation, we have

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \qquad \ldots(14.13)$$

where d_1 is the density of liquid I and t_1, is time of flow of liquid 1 of coefficient of viscosity η_1. d_2, t_2 and η_2 are the corresponding quantities for liquid 2.

Units of viscosity. CGS units of viscosity are dyne second —cm^{-2} or dyne-second per cm^2, SI units are newton-second-metre^{-2} or N-sec-m^{-2}. The CGS unit for coefficients of viscosity is the poise. It is found to be a rather large unit and therefore in experimental work smaller units of centipoise (10^{-2} poise) millipoise (10^{-3} poise) and micropoise (10^{-6} poise) are also used. One SI unit of viscosity equals 10 poise. Commonly used apparatus for the measurement of viscosity is Ostwald viscometer. For any liquid the viscosity is found to diminish with increasing temperature. The viscosity of a liquid decreases by about 1 to 2 per cent for each degree rise in temperature. The reciprocal of viscosity is called fluidity Fig 14.7 shows the variation of coefficent of viscosity with temperature.

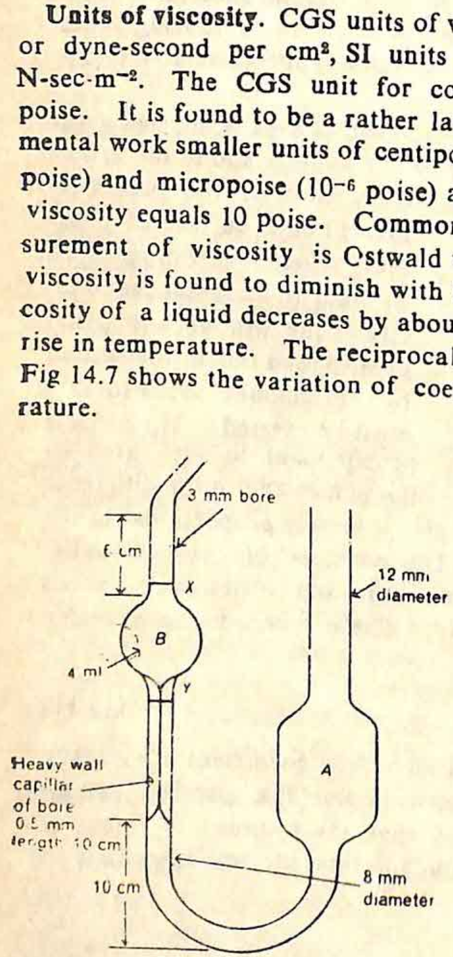


FIG.14.6
Ostwald Viscometer.

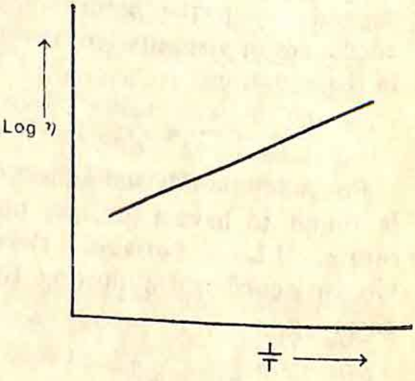


FIG. 14.7
Effect of temperature on viscosity.

The variation of viscosity with temperature follows fairly closely the Andrade equation, i.e.,

$$\eta = Ae^{B/RT}$$

where A and B are constants for a given liquid. B is the activation energy. It is probably related to the work needed to form "holes" in the liquid into which molecules can move, thus permitting relative motion to take place. Viscosity of a liquid depends on molecular size, and, particularly, length and also on the magnitude of the inter-molecular forces. Non-polar liquids (e.g., cylohexane, toluene) generally have low viscosity. Whereas liquids in which directed bonding can occur between the molecules have relatively high viscosities.

Exercise 14.2. *To determine the coefficient of viscocity of a liquid (benzene or carbon tetrachloride).*

Material required. 1. Ostwald viscometer.

2. 10ml graduated pipette.
3. Stop clock.
4. Specific gravity bottle.
5. Clamp.

Procedure. Thoroughly clean the viscometer with warm chromic acid, rinse several times with distilled water and dry it. Introduce into the viscometer by means of pipette, a known volume of distilled water sufficient for one meniscus to be in the lower part of bulb A (Fig. 14.6). Now suck the liquid in the bulb B through a rubber tube attached to C to a level above the mark x. Clamp the viscometer vertically and allow the water to flow freely through the capillary and note the time t_w on a stop-clock for the flow of water from x to y. Repeat two more observations with distilled water. The three values of t_1 should be concordant to one second or better.

Drain the water from the viscometer, rinse twice with acetone and dry by blowing air through it. Indroduce exactly the same volume of the given liquid in the same manner as was done with distilled water. Let t_l be the time taken for the flow of given liquid from x to y.

Determine the densities of the liquid and of water with the help of a specific gravity bottle and also note down the temperature of measurement. For measurements at different temperatures a thermostat with an adjustable temperature should be employed. Note down the viscosity of water at the temperature of measurements from the table in the appendix.

Record of observations:

Temperature = ...°C

Density of water at °C, d_w = g/c.c.

Viscosity of water at t °C, η_w = milli poise

Weight of the empty specific gravity bottle = W_1 g,

Weight of the specific gravity bottle + liquid = W_2

Weight of the specific gravity bottle + water = W_3 g

Method of calculation:

Density of the liquid, $d_l = \frac{W_2 - W_1}{W_3 - W_1} \times d_w$

d_w is the density of water noted from the tables

Coefficient of viscosity $\eta_l = \frac{\eta_w \times d_l \times t_l}{d_w \times t_w}$

Result. The coefficient of viscosity of the given liquid was found to be......milli poise.

Exercise 14.4 – *To determine the concentration of the unknown solution of glycerol – Water.*

Procedure.—Determine the time of flow for pure glycerol and pure water. Prepare three solutions A, B and C in the following manner. Solution A (15.00 ml glycerol + 5.00 ml water) solution B (10.0 ml glycerol + 10.0 ml water) and solution C (5.00 ml glycerol + 15.00 ml water). Determine the time of flow in each case. Plot a graph between the time of flow and the percentage composition. Determine the time of flow for the unknown solution. From the straight line graph determine the concentration of the unknown solution.

15

Solid State and Transition Temperature

Crystals have held an unusual fascination for laymen and scientists throughout history. Diamonds, rubies, emralds and other gemstones are liked by everyone due to their colour, beauty and stability of their crystals.

A crystalline solid is characterised by the three criteria:

(*i*) a definite melting point,

(*ii*) a definite heat of fusion,

(*iii*) a definite crystal lattice.

Whether a given substance is crystalline or amorphous can be decided only by examining it under a microscope. A perfect crystal has a perfectly periodic structure.

15.1. CRYSTALLOGRAPHY

It is the science of crystals which deals with the study of their development, growth and their external form. It is based on three fundamental laws.

(*i*) Steno's law of constancy of interfacial angles,

(*ii*) Hauy's law of rationality of indices,

(*iii*) The law of symmetry.

We shall learn to verify the law of constancy of interfacial angles. The law states, that for a given substance the corresponding face or planes forming the external surfaces of a crystal always intersect at a definite angle and this angle always remains constant, no matter how the crystals develop.

Exercise 15.1. *To determine the interfacial angles of (a) Calcite, (b) Quartz, crystals, with the help of a contact goniometer and verify the law of constancy of interfacial angles.*

Principle. The contact goniometer (Fig. 15.1) is the simplest instrument used to measure the interfacial angles of a crystal. This consists of a graduated semi-circular protector fitted with a movable arm and a pair of slotted bars fitted with straight edges. By moving the pivoted arm any angle between the two faces can be easily adjusted and measure on the protector.

Working. As stated earlier that what ever may be the shape of

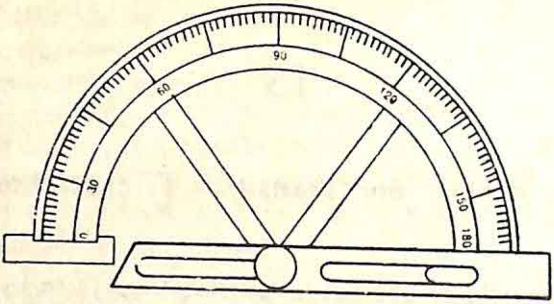


FIG. 15.1

the crystal the interfacial angle between the corresponding faces of the crystal is always same. Fig 15.2 represent the geometry of calcite and quartz crystals respectively. To measure the

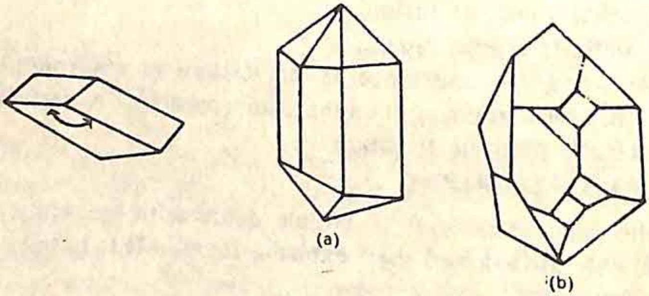


FIG. 15.2

interfacial angle hold the crystal firmly in between the two straight edges of the pair of slotted bars so that they are in close contact with the two faces of the crystal for which the interfacial angle is to be determined. (See Fig 15.3).

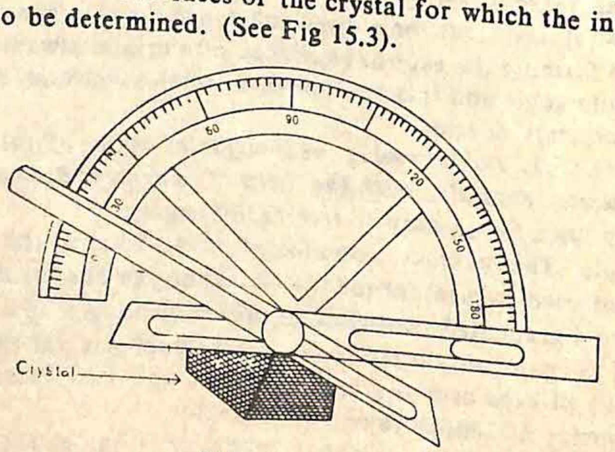


FIG. 15.3

Adjust carefully the straight edges and tight the pivoted screw of the goniometer. Remove the crystal carefully without disturbing the position of the movable arm and read the angle on the semi-circular protector. This angle corresponds to the interfacial angle between the corresponding faces of the crystal. Record this and measure all the interfacial angles using same method. Now break the crystal to a smaller size and again measure the angles and compare the angles obtained with the values already determined. This is observed that the interfacial angles show a behaviour of constancy even after the crystal has been broken to a smaller size. This can be easily seen with calcite crystals, but the quartz crystals are very hard so the law can be verified by taking 2 or 3 crystals and measuring their angles.

15.2. TRANSITION TEMPERATURES

There are numerous elements and compounds which are known to exist in more than one crystalline form that are stable in different temperature ranges. One of the well known example is sulphur. Sulphur exists in rhombic form below 96°C and above this temperature the rhombic form passes into monoclinic form, i.e.,

$$\text{S (rhombic)} \overset{96°\text{C}}{\rightleftharpoons} \text{S(monoclinic)}$$

At 96°C the two forms can co-exist and remain in equilibrium with each other, and this is known as the transition temperature.

Transition temperature. The temperature at which two crystalline forms of a substance can remain in equilibrium with each other at a pressure of one atmosphere is called its transition point or transition temperature.

Such substances are known as polymorphous substances. Transition temperatures are also observed in salt hydrates. Here the hydrated form and the anhydrous form or a lower hydrate remain in equilibrium. The anhydrous salt and the hydrated salt have different solubility characteristics. The solubilities of the two forms vary in different ways with the rise in temperature. Therefore, the one simple method of determining the transition temperature is to determine the solubility of the given salt at different temperatures and from the graph thus plotted, transition temperature can be determined.

Transition temperatures of a few salt hydrates have been given as follows:

$$Na_2SO_4.10H_2O \overset{32.40°\text{C}}{\rightleftharpoons} Na_2SO_4+10H\ O$$

$$Na_2CO_3.7H_2O \overset{32.31°C}{\rightleftharpoons} Na_2CO_3+7H_2O$$

$$NaBr.2H_2O \overset{50.78°C}{\rightleftharpoons} NaBr+2H_2O$$

$$SrCl_2.6H_2O \overset{61.34°C}{\rightleftharpoons} SrCl_2+6H_2O$$

The commonly used methods of determining the transition temperature are the following:

(*i*) Thermometric method.

(*ii*) Dilatometric method.

(*iii*) Solubility method.

Exercise 15.2. *To determine the transition temperature of sodium sulphate decahydrate* ($Na_2SO_4.10H_2O$).

Principle. The hydrated sodium sulphate exists in the euqilibria,

$$Na_2SO_4.10H_2O \rightleftharpoons Na_2SO_4+10H_2O$$

when such a system is allowed to cool slowly from above the transition point. When this point is reached the temperature remains constant for some time.

Materials required. A thin glass tube, two thermometers, stirrer, and sodium sulphate ($Na_2SO_4.10H_2O$)

Procedure. Take about 20 to 25 g of recrystallized sodium sulphate ($Na_2SO_4.10H_2O$) in a thin walled glass tube. Insert a 100°C thermometer and stirrer. Suspend this assembly in a 400ml beaker containing water. A thermometer is also placed inside the water in the beaker (See Fig. 15.4). Heat the water slowly and keep the temperature uniform with a stirrer. Stop heating when the temperature reaches 30°C and maintain it at this temperature for nearly 10 minutes. Now raise the temperature of the bath slowly at the rate of 1°C in 5 minutes and record the temperature of the partially liquified mass after every half a minute. A stage will then be reached at which the thermometer will show a practically stationary reading for sometime before it starts rising again. Record the temperature readings up to 37°C.

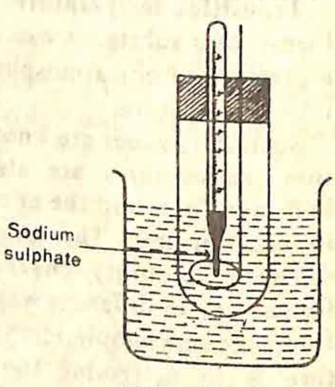


FIG. 15.4

Now allow the hot solution to cool slowly while the solution is kept stirred. Note the thermometer readings after every half a minute. Continue to record the temperature until it falls to 30°C. During cooling, a stage will again be found when the temperature will remain constant for sometime.

Observations and calculation.

Time (*minutes*)	*Temperature* °C	*Time* (*minutes*)	*Temperature* °C
...	...	...	...
...	...	...	...
...	...	...	...
...	...	...	...
...	...	...	...

Plot a graph of temperature of the mixture in test tube versus time both for rising and falling temperature as in Fig. 15.5.

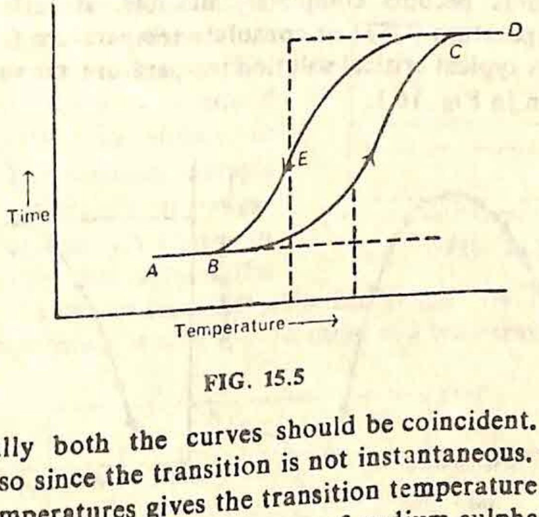


FIG. 15.5

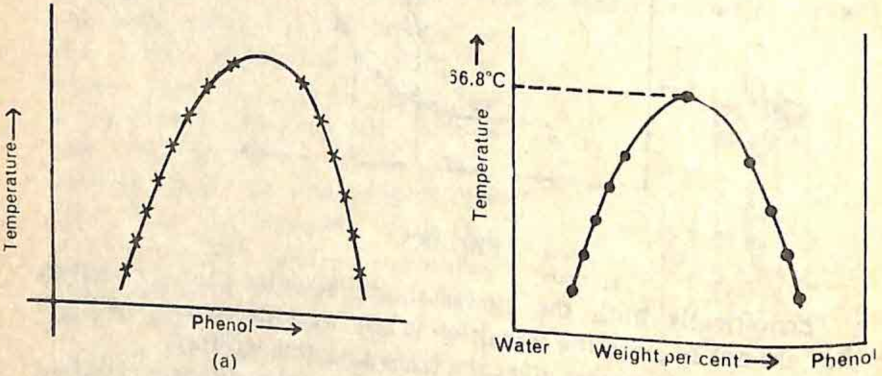
Theoretically both the curves should be coincident. However, they are not so since the transition is not instantaneous. The mean of the two temperatures gives the transition temperature.

Result. The transition temperature of sodium sulphate ($Na_2SO_4.10H_2O$) was found to be ...... °C.

16

Heterogeneous Equilibrium

When ether is shaken with water a definite amount of the ether dissolves in water, similarly a small amount of water dissolves in the ether. Thus we get two liquid solutions the composition of which depends on the temperature. Usually the solubility increases with the increase in temperature. At each temperature there will be two solubility values one representing the solubility of ether in water and the other the solubility of water in ether. Between the temperatures of their boiling points and freezing points two liquids may be completely miscible, partially miscible or completely immiscible. The temperature, at and above which two partially miscible liquids become completely miscible, is called its critical solution temperature (CST) or consolute temperature for the given liquid pair. A typical critical solution temperature curve for Phenol-water is given in Fig. 16.1.



(a)

(b)

FIG. 16.1. (*a*) and (*b*) Phenol-water System.

When phenol and water are shaken together at room temperature two saturated solutions, i.e., a solution of phenol in water and a solution of water in phenol, are obtained. These coexisting solutions are known as conjugate solutions and will have the same vapour pressure. Three types of liquid pairs are obtained in actual practice, i.e., (*i*) with increasing mutual solubility, (*ii*) with decreasing mutual solubility, and (*iii*) with closed mutual solubility.

1. **Type with increasing mutual solubility.** Phenol-water system is a well known example under this category. On increasing the temperature, the mutual solubility of two liquids in the two layers increases until at certain temperature, the compositions of the two layers become same. Above this temperature the two liquids are completely miscible. The curve is a parabola similar to the one shown in Fig. 16.1. Other examples of systems with upper CST are:

(*i*) Aniline-hexane, 59.6°C.

(*ii*) Methyl alcohol-carbon disulphide, 40.5°C.

(*iii*) Benzene-sulphur, 163°C.

2. **Type with decreasing mutual solubility.** There are certain systems in which the mutual solubility decreases with increasing temperature. Such systems are said to have a lower CST, as shown in Fig. 16.2. The common example is triethylamine-water system.

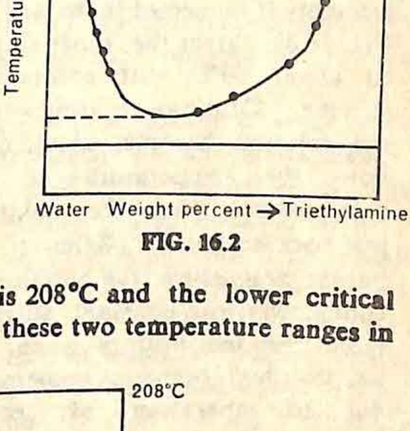


FIG. 16.2

3. **Type with closed mutual solubility.** In some systems both upper and lower critical solution temperatures are exhibited. For such systems there is a closed solubility curve as shown in Fig. 16.3. The common example under this category is nicotine-water system is shown in Fig. 16.3. For this system the upper critical solution temperature is 208°C and the lower critical solution temperature is 60.8°C. In these two temperature ranges in

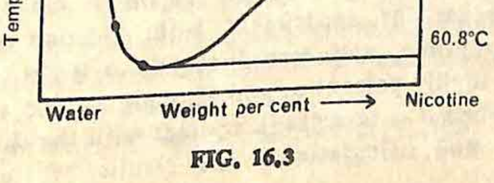


FIG. 16.3

the enclosed area, the two liquids are partially miscible but outside the ranges, these are completely miscible.

Effect of impurities on critical solution temperature. The impurities have a marked effect on the critical solution temperature. Crismer found that if a substance dissolves in one of the two liquids, the upper critical solution temperature rises and the lower critical solution temperature decreases. On the other hand if a substance dissolves in both the liquids, the upper critical solution temperature will be lowered and the lower critical solution temperature will rise. Since CST is very sensitive to the presence of impurities it can be used as a criteria of purity.

Exercise 16.1. *To determine the critical solution temperature and composition of solution at the CST for Phenol-water system.*

Materials required. Phenol, water, hard glass test tube, thermometer, stirrer, outer glass jacket.

Procedure. Weigh 8.0 g of phenol in a weighing tube and transfer to the hard glass test tube, *A*. Add to it 7 ml of distilled water with the help of a graduated pipette. This is then fitted in an outer jacket *B*, and the whole assembly is immersed in water (See Fig. 16.4). Heat the water slowly to about 60°C with continuous stirring. Continue heating until the solution becomes clear, note down the temperature in the thermometer when the solution just becomes clear. Remove the burner and allow the solution to cool slowly with constant stirring. Note the temperature when the solution just becomes opalescent, due to separation of second phase. Add two ml of distilled water to the test tube. Heat the solution and again record the temperature at which the solution becomes clear and then opalescent. Repeat the experiment with addition of 2ml of distilled water everytime, and record seven to eight observations. Since phenol is highly poisonous and strongly caustic and produces painful burns when it is brought in contact with the skin.

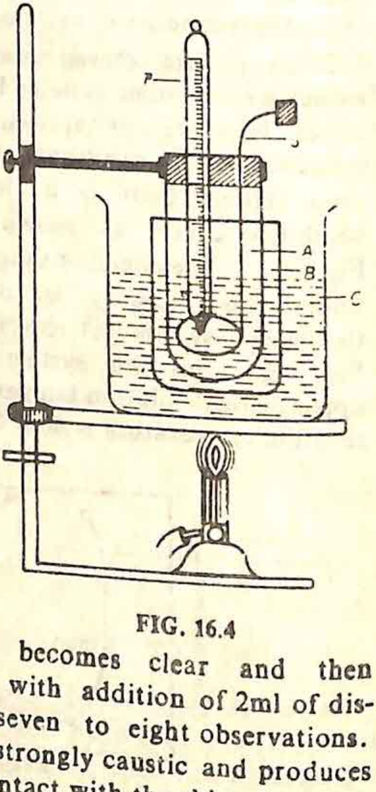


FIG. 16.4

Observations and calculation: The results are as shown in the Table 16.1.

Room temperature= °C

Density of water at room temperature= g/ml

Weight of Phenol=8.0g.

TABLE 16.1

Sl. No.	*Weight of water (x gm)*	*Percentage by weight of phenol* $\frac{8}{8+x}\times 100$	*Miscibility temperature*		
			Opalescence disappears t_1°C	*Opalescence appears* t_2°C	*Average* $\frac{t_1+t_2}{2}$°C
1.	...	...	...	...	...
2.	...	...	...	...	...
3.	...	...	...	...	...

Plot the miscibility temperature versus composition for the above data and calculate the CST for phenol-water system and the composition of the solution.

Perform the experiments with (*i*) cyclohexane-methanol, (*ii*) aniline-hexane and determine CST and the composition in each case.

Exercise 16.2. *To study the effect of sodium chloride as an impurity on critical solution temperature of phenol-water system.*

Materials required. Phenol, distilled water, thermometer, hard glass test tube, outer glass jacket, stirrer, sodium chloride solution.

Procedure. Weigh 8 g of phenol in a weighing tube and transfer it to a hard glass test tube *A*. Add 7 ml of distilled water with the help of graduated pipette. This is then fitted in an outer jacket *B* and the whole assembly is immersed in water. Continue heating until the solution becomes clear. Note the temperature. Remove the burner and stir the solution to cool slowly. Note the temperature when the solution just becomes opalescent, due to the separation of the second phase. Add 2ml solution of 1 per cent sodium chloride. Heat the solution and record the miscibility temperature, in the same manner. Continue the addition of 2 ml sodium chloride solution and record the miscibility temperature.

Observations and calculation: Room temperature = °C

Weight of phenol=8 g.

Density of water at room temperature= g/ml.

TABLE 16.2

Sl. No.	*Percentage of NaCl*	*Miscibility temperature*		
		Opalescence disappears °C	*Opalescence appears °C*	*Average °C*
1.	...	...	...	...
2.	...	...	...	...
3.	...	...	...	...

Plot a graph of miscibility temperature versus the percentage of salt in solution. Discuss the effect of sodium chloride impurity on phenol-water CST.

16.1. SOLID-LIQUID SYSTEMS

When a liquid is allowed to cool in steady surroundings and if we plot a graph between temperature and time, the graph line is called the cooling curve. A cooling curve will thus be a curved line whose slope will progressively decrease. If during the process of cooling of a liquid a solid phase separates out, i.e., the liquid reaches its freezing point, see Fig. 16.5.

If there is no supercooling, the composition of the solid depends on the nature of two components. The equilibrium temperature, i.e., the freezing point depends only on the composition of the liquid and not on the relative amounts of liquid and solid. When the solid separating out has the same composition as the liquid phase then no change in the composition of the liquid occurs during freezing and as a consequence of this, freezing point remains constant during the change. This condition applies to the separation of solid from a pure liquid and the separation of a mixture or compound with congruent melting point from a binary liquid mixture. If on the other hand, the composition of the solid phase differs from that of the liquid then the freezing temperature will change as more of the solid separates out. The method of thermal analysis involves the study of the

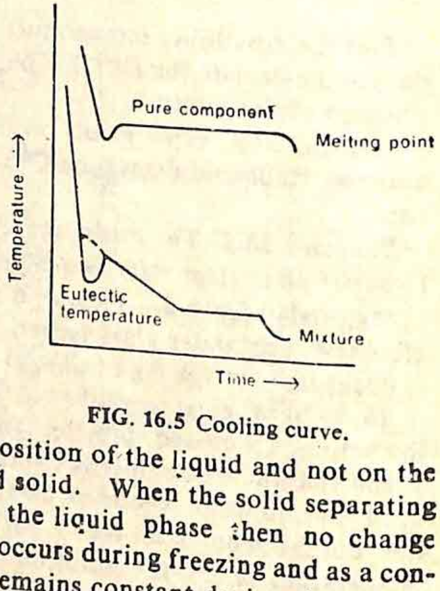


FIG. 16.5 Cooling curve.

cooling curves obtained when a liquid mixture is cooled. The cooling curve will have any one of the shapes in Fig. 16.6. (*a*), (*b*) and (*c*).

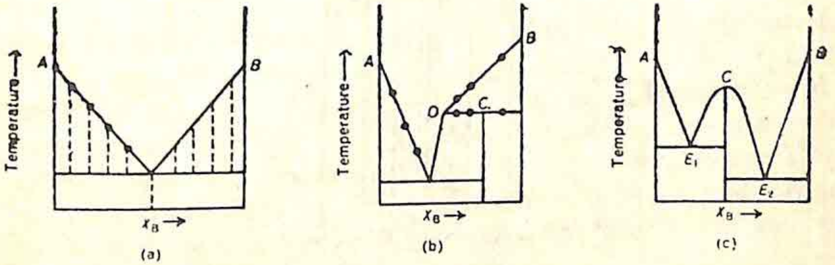


FIG. 16.6

Exercise 16.3. *To determine the freezing point curve for mixtures of o-nitrophenol and p-toluidine.*

Materials required. Test tubes, boiling tube, thermometer (up to 360°C), stirrer.

Procedure. Prepare the mixtures of o-nitrophenol and p-toluidine, as shown in Table 16.3.

TABLE 16.3

Components	*Weight in grams*										
o-nitrophenol	10	9	8	7	6	5	4	3	2	1	0
p-toluidine	0	1	2	3	4	5	6	7	8	9	10

Take the mixtures in the ratio indicated in Table 16.3, in a hard glass test tube fitted with a thermometer. Immerse, this in a water bath. Heat and stir the mixture till it melts. Take out the test tube, wipe it clean and put this in a boiling tube which provides an air jacket see Fig. 16.7. Stir the mixture and note its temperature after every half minute. Note down the temperature at which solid just begins to form, and when the liquid-solid system shows temperature halt.

Repeat the experiment with other compositions of the mixture (Table 16.4) and plot the cooling curves in each case.

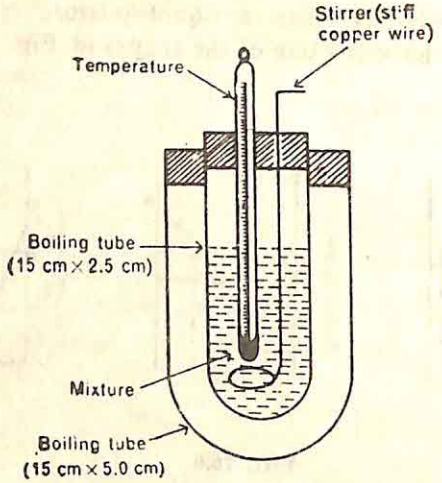

Stirrer (stiff copper wire)
Temperature
Boiling tube (15 cm × 2.5 cm)
Mixture
Boiling tube (15 cm × 5.0 cm)

FIG. 16.7. Apparatus for determining cooling curve.

Observations.

TABLE 16.4

Sl. No.	*Percentage of p-toulidine*	*Freezing point °C*	*Temperature halts*
1.	...	...	...
2.	...	...	...
3.	...	...	...

Repeat the experiment with following sets of mixtures, i.e., (*i*) Benzoic acid—Cinnamic acid, (*ii*) Naphthalene-Benzoic acid, (*iii*) Naphthalene-β-naphthylamine. Plot the cooling curves in each case and discuss the phase diagram.

16.2. DISTRIBUTION OF SOLUTES BETWEEN TWO IMMISCIBLE LIQUIDS

Solubility and the effects of the solute on the properties of the solution, have so far been discussed in terms of simplest system, of one solvent and one solute. If the solvents are miscible, the solubility may be taken, to a first approximation, to be the mean of the solubilities in the separate solvents. When the solvents are immiscible, or nearly so, the situation is greatly simplified. The solute distributes itself between a pair of solvents according to the partition or distribution law, which states that the ratio of concentrations in the two solvents at equilibrium is a constant, known as the partition or distribution coefficient, K, i.e.,

$$\frac{C_A}{C_B}=K \qquad \ldots (16.1)$$

where C_A and C_B are the concentrations of the solute in the solvent A and B respectively in any units. This is known as Nernst's Law. The law does not apply if the temperature is not constant throughout the system, or if, in either solvent, the solute associates, dissociates, ionises or reaches its solubility limit. Strictly speaking, the law is valid for ideally dilute solutions. If in the second solvent the solute is associated and n is the degree of association, we can write,

$$\frac{C_A}{\sqrt[n]{C_B}}=K \qquad \ldots (16.2)$$

If the solute dissociates in the solvent of concentrations C_B and α is the degree of dissociation, we can write,

$$\frac{C_A}{C_B\,(1-\alpha)}=K \qquad \ldots (16.3)$$

Exercise 16.4. *To determine the partition coefficient of iodine in carbon tetrachloride and water.*

Materials required. Five stoppered bottles, pipette (10 ml), conical flask, iodine, carbon tetrachloride, 0.1 N and 0.01 N sodium thiosulphate solutions, glass trough, thermometer.

Procedure. Prepare a saturated solution of iodine in carbon tetrachloride and filter. Take five 200ml capacity glass stoppered bottles and label them 1, 2, 3, 4, 5, and make the following mixtures as in, Table 16.5.

TABLE 16.5

Bottle No.	*Volume of saturated iodine solution in CCl_4 (ml)*	*Volume of CCl_4 (ml)*	*Volume of water (ml)*
1.	30	0	100
2.	25	5	100
3.	20	10	100
4.	15	15	100
5.	10	20	100

Stopper the bottles, shake them vigorously, and place in a trough of water for about 30 minutes. Shake the contents from time to time. Note down the temperature of water. In this case the upper layer will be aqueous layer and lower layer will be iodine solution in carbon tetrachloride.

Titration of the aqueous layer. Pipette out 5ml of the carbon tetrachloride layer into a conical flask containing about 25ml of distilled water. The addition of water helps in extracting iodine into water layer where it reacts with 0.1 N sodium thiosulphate using starch as indicator. Record at least two concordant readings. Titrate the organic layers in bottles numbered 2, 3, 4 and 5. Record your observations as shown in Table 16.6. Calculate the ratio $\frac{C_{org}}{C_{aq}}$ which will be constant.

Observations. Temperature=...°C.

TABLE 16.6

Sl. No.	*Volume of 0.01 N $S_2O_3^{2-}$=20ml aqueous layer* (ml)	*Concentrations of I_2 in aqueous layer (normality)* C_{aq}	*Volume of $S_2O_3^{2-}$=5ml of organic layer (ml)*	*Concentration of I_2 in organic layer (normality) (ml)* C_{org}	$\frac{C_{org}}{C_{aq}}=K$
1.	...	...	...	...	...
2.	...	...	...	...	...
3.	...	...	...	...	...
4.	...	...	...	...	...
5.	...	...	...	...	...

Result. The partition coefficient of iodine between carbon tetrachloride and water=.........

Exercise. 16.5. *To determine the partition coefficient of iodine between benzene and water.*

Procedure. Same procedure as in Exercise 16.4.

Exercise 16.6. *To determine the partition coefficient of iodine between chloroform and water.*

Procedure. Same procedure as in Exercise 16.4.

Exercise 16.7. *To study the partition coefficient of benzoic acid between benzene and water.*

Materials required. 5 stoppered bottles, benzoic acid, benzene 0.1 N-NaOH, pipette, thermometer.

Procedure. Prepare a saturated solution of benzoic acid in benzene and filter. Take five 200ml capacity glass stoppered bottles and label them 1, 2, 3, 4, and 5. Prepare the following mixtures in them, Table 16.7.

TABLE 16.7

Bottle No.	*Volume of saturated benzoic acid solution (ml)*	*Volume of benzene (ml)*	*Volume of water (ml)*
1.	30	0	100
2.	25	5	100
3.	20	10	100
4.	15	15	100
5.	10	20	100

Stopper the bottles, shake them vigorously and place them in a trough of water for about 30 minutes. Shake the bottles from time to time. Note down the temperature of water. In this case the upper layer will be benzene layer and the lower layer will be water layer.

Titration for the organic layer. Pipette out 5ml of the organic layer (benzene layer) into a conical flask containing about 25ml of distilled water. Titrate with 0.1 N-NaOH using phenolphthalein indicator, shake the solution vigorously during titration. Record at least two concordant readings. Similarly titrate the organic layers in the bottle Nos. 2, 3, 4, and 5.

Titration of the aqueous layer. Pipette out 20ml of the aqueous layer from bottle No. 1 into a conical flask. Titrate this with 0.1 N NaOH using phenolphthalein indicator, shake the solution during titration. Record at least two concordant readings. Repeat the titration with bottle Nos. 2,3,4, and 5. Record the observations as in Table 16 8. Calculate the ratio and find out the constant values of the partition coefficent.

Observations and calculation.

TABLE 16.8

Bottle No.	*Volume of 0.1 N-NaOH for 5ml organic layer (ml)*	*Concn. of acid in organic layer in C_{org}*	*Volume of 0.1 N-NaOH for 20ml v/l aqueous layer (ml)*	*Concn. of acid in aqueous layer in gm equiv/liter C_{aq}*	$\frac{C_{org}}{C_{aq}}$	$\frac{\sqrt{C_{org}}}{C_{aq}}$
1.	...	...	...	...	...	...
2.	...	...	...	...	...	...
3.	...	...	...	...	...	...

17

Thermochemical Measurements

Introduction

Most chemical processes are accompanied by a measurable absorption or evolution of heat. Thermochemistry involves the measurement of heat changes in some physical chemical processes. The thermochemical measurements are based on the first law of Thermodynamics, which states that energy can be changed from one form to another it cannot arise out of nothing nor it can disappear into nothing. When a system undergoes a change such as the compression of a gas or melting of a solid or a chemical reaction, the internal energy change ΔE of the system is given according to relation (1), i.e.,

$$\Delta E = Q - W$$

where Q is the heat absorbed and W is the work done by the system. Each chemical reaction has associated with it an energy change which is characteristic of the reaction and is proportional to the increase in internal energy ΔE. It follows from the First Law of Thermodynamics that the magnitude of the heat change is proportional to the quantity of substance and products, but is independent of the path followed by the reaction. This is known as Hess's Law. Determination of the amount of heat used or produced in a chemical reaction or a physical change is usually carried out by measuring the change in temperature. This is known as Calorimetry.

The experimental measurement of a reaction heat, the reaction is carried out in a well-insulated vessel, known as calorimeter. Since it is insulated, it can effectively measure the heat energy transferred during a reaction.

Dewar flask is commonly used as calorimeter as shown in Fig. 17.1. It has a large heat capacity. The inner surface of the vessel is silvered and a space between the inner and outer walls is evacuated in order to minimise exchange of heat energy with the surroundings. A cork stopper is fitted at the top of the mouth and it contains a thermometer.

Heat is measured in calories. The gram-calorie is the amount of heat required to raise the temperature of 1 g of water through 1°C. For accurate measurements, degree is specified in 14-15° C. The amount of heat evolved in a process can be measured as, mass of system × rise in temperature × specific heat of the system.

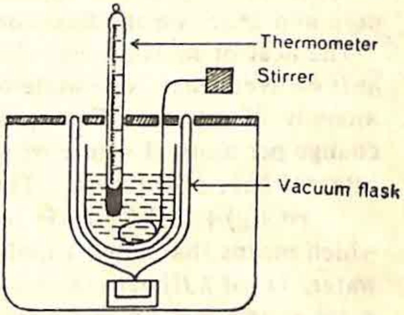


FIG. 17.1. Dewar flask.

Water equivalent of a calorimeter. The technique of calorimetry presents two principal difficulties: (*i*) how to determine the heat capacity of the calorimeter and all its contents, (*ii*) to deal with the inevitable heat exchange between calorimeter and its surroundings. Water-equivalent of a calorimeter may be defined as the amount of heat required to raise the temperature of the calorimeter by 1°C. For most practical purposes glass beaker serves as a calorimeter, in such a case it is not practicable to obtain water equivalent by multiplying mass and specific heat of the material of the vessel, the water equivalent value can be found for such part of the vessel as is usually in contact with the reacting system.

The water equivalent of a glass beaker is found by supplying a known amount of heat to the system and determining the rise of temperature, which it produces. Equal volumes are used as far as possible so that the area of the calorimeter in contact with the system does not change.

Simple experiments in thermochemistry will be given here, i.e., measurement of heat of solution and heat of neutralisation.

17.1. HEAT OF SOLUTION

When a solute is dissolved in a solvent to form a solution there is often either evolution or absorption of heat. Generally speaking, hydrated salts and salts which do not form hydrates dissolve in water with absorption of heat or with a very small evolution of heat, but the solution of anhydrous salts which form hydrates, is frequently accompanied by evolution of heat, the combination of salt with water being an exothermic process. Since the process of dilution is generally accompanied by a heat effect, known as heat of dilution. Hence, the heat of solution or the amount of heat absorbed or evolved when 1 g-molecule of substance is dissolved, depends on the amount of solvent used and hence on the final concentration of the solution produced.

The heat of solution may therefore be defined as the amount of heat evolved when one mole of solute is dissolved in a specified amount of solvent. For quantitative expression, the total heat change per mole of solute when solution is complete is called the integral heat of solution. This can be indicated as follows:

$$HCl(g)+50H_2O(l)=HCl\ 50H_2O,\ \triangle H=-73kJ\ mol^{-1}$$

which means that when 1 mole of HCl is dissolved in 50 moles of water, 73 of kJ heat are evolved. The heat of solution values of some salts are given in Appendix A-6.

Differential heat of solution. Differential heat of solution of a substance at a specified concentration of a solution for a specified constant temperature and pressure conditions, is change in enthalpy observed per further mole of solute dissolved in such a large quantity of solution that no significant change in concentration of solution occurs.

Heat of neutralisation. When a base is added to an acid it neutralises the acid and heat is evolved in the process. Heat of neutralisation of an acid by a base is defined as the amount of heat evolved when 1 gram-equivalent of the acid is neutralised by a base.

For strong acids and bases the value of heat of neutralisation is constant and equal to about 13.7k cal.

Consider the neutralisation of a strong acid by a strong base, i e., HCl by NaOH. The chemical reaction can be symbolised as:

$$Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H_2O$$

$$\text{or } H^+ + OH^- \rightarrow H_2O$$

This shows that the neutralisation of a strong acid by a strong base involves the combination of H^+ ions of the acid with OH^- ions furnished by a base and should not depend on the identities of the particular acid and base involved. It follows therefore that the heat of neutralisation of all strong acids by strong alkalis in dilute solution should be practically the same as shown in Table 17.1.

TABLE 17.1

Heat of Neutralisation Values

Acid	*Alkali*	*Heat of Neutralisation (k-cal)*
HCl	NaOH	− 13.68
HNO_3	NaOH	− 13.69
HCl	LiOH	− 13.70

If one of the reactants in an acid-base reaction is a weak electrolyte the heat of neutralisation is not the same. The difference is primarily due to the dissociation of the weak electrolyte.

Exercise 17.1. *To determine the water equivalent of a calorimeter.*

Procedure. Take 50ml of cold water in a 250ml beaker and keep it in a thermosflask. Note down the temperature after every one minute for five minutes let it be t_1°C. In another beaker heat 50ml of water to t_2°C. Add this water to the beaker in the thermosflask. Stir and note down its temperature after every one minute with a stop clock, calculate the final temperature t°C from the plot of temperature versus time see Fig. 17.2. interpolating it backward.

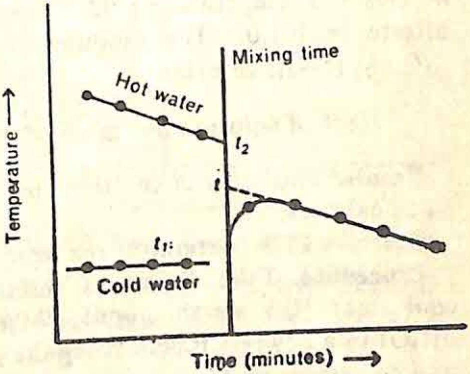


FIG. 17.2. Water equivalent of Calorimeter.

Method of calculation. The water equivalent of a calorimeter, W can be calulated as follows:

Heat lost by hot water = Heat gained by cold water and calorimeter.

i.e., $m_2 \times s(t_2 - t) = m_1 \times s(t - t_1) + W(t - t_1)$

m_1 = mass of cold water,
m_2 = mass of hot water,
W = water equivalent of calorimeter,
s = specific heat of water.

For water $s = 1$

$$m_2(t_2 - t) = m_1(t - t_1) + W(t - t_2)$$

$$\text{Water Equivalent of Calorimeter } W = \frac{m_2(t_2 - t) - m_1(t - t_1)}{(t - t_1)} \text{g.}$$

Result. The water equivalent of calorimeter = ...g. Its value can be expressed as the number of grams of water which have the same heat capacity as the calorimeter.

Exercise 17.2. *To determine the heat of solution of potassium nitrate.*

Procedure. Take 100ml of water in a 250ml beaker whose water equivalent (W) has been determined. Weigh about 4.0 g of potassium nitrate in a dry test tube. Keep the beaker in a thermosflask stir it and note the temperature (t_1) after every half minute till it becomes constant. Transfer quickly potassium nitrate in the flask.

Stir the solution with a stirrer. Note down the temperature of the solution after half a minute and go on measuring the temperature, for about 10 minutes. Determine the final temperature (t) of the solution by interpolating the temperature time graph to the temperature when potassium nitrate was just dissolved.

Method of calculation. Let m_s be the weight of potassium nitrate added in m_1 gms of water in a calorimeter of water equivalent W gms at a temperature t_1°C. The molecular weight of potassium nitrate is 101.0. The amount of heat envolved or absorbed $Q=(W+m_1)(t-t_1)$ calories.

$$\text{Heat of solution per mole of solute}=\frac{Q\times 101.0}{m_s}\text{ calories.}$$

Result. The heat of solution per mole of potassium nitrate. . . . . . . calories.

Exercise 17.3. *Determine the heat of solution of copper sulphate.*

Procedure. Take 100ml of water in a 250ml beaker of water equivalent (W) weigh about 10.0g of copper sulphate ($CuSO_4.5H_2O$) in a dry test tube. Keep the beaker in a thermosflask, stir and determine its temperature at an interval of half minute, for 4-5 minutes. Transfer quickly copper sulphate in the thermosflask and stir it, using glass stirrer. Note temperature readings, after every half minute. Determine the final temperature of the mixture from the temperature-time graph.

Method of calculation. Let m_s be the weight of copper sulphate added in m_1 g of water in a calorimeter of water equivalent W g. at a temperature t_1°C. Let t be the final temperature of the mixture. The molecular weight of $CuSO_4.5H_2O$ is 249.5.

The amount of heat evolued or absorbed $Q=(W+m_1)(t-t_1)$ ...k calories.

$$\text{Heat of solution per mole of solute}=\frac{Q\times 249.5}{m_s}$$

Result. The heat of solution of copper sulphate per mole . . . calories.

Exercise 17.4. *Determine the heat of neutralisation of hydrochloric acid and sodium hydroxide.*

Procedure. Determine the water equivalent of a calorimeter as described in Exercise 17.1. Prepare N-NaOH and N-HCl solutions. Standardise sodium hydroxide by titrating against oxalic acid. Hydrochloric acid is standardised by titrating against sodium hydroxide solution. Measure 50ml of N-HCl in a 250ml beaker and place it in a thermosflask. Note the temperature after every half minute for five minutes. In another beaker measure 50ml of N-NaOH and note the temperature after every half minute for five minutes. Pour it in a thermosflask and stir the solution vigorously. Note the reading of the thermometer kept in the solution after an interval of half minute, for five minutes. At the end of the experiment take out the beaker from the thermosflask and add a drop of phenolphthalein formation of a pink colour confirms complete neutralisation. Plot a graph of temperature versus time (See Fig 17.3) and from the graph calculate the temperature of mixing.

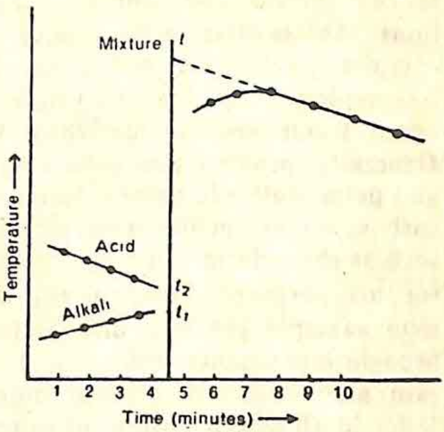


FIG. 17.3. Radiation correction for curves·

Method of calculation. Let W g be the water equivalent of calorimeter, t_1 is the temperature of acid and t_2 be the temperature the base before mixing and t be the result temperature of the solution. The heat evolved in the neutralisation reaction:

$$Q=(W+100)\left(t-\frac{t_1+t_2}{2}\right)$$

Result. The heat of neutralisation of strong acid strong base was found to be . . . . *k* cals.

Exercise 17.5. *To determine the heat of ionisation of* CH_3COOH *and* NH_4OH.

Procedure. (*i*) Measure the heat of neutralisation of CH_3COOH and NaOH in IM solutions. The heat of ionisation of acetic acid is given by the relation:

Heat of ionisation of $CH_3COOH = 13.7 -$ Heat of neutralisation of CH_3COOH against NaOH.

(*ii*) Heat of ionisation of NH_4OH can be found by measuring experimentally the heat of neutralisation of IM-NH_4OH against IM-HCl.

Heat of ionisation of $NH_4OH = 13.7 -$ Heat of neutralisation of NH_4OH against HCl.

17.2. SOLUBILITY

Solutions of Solids in Liquids. Several types of solutions may be prepared by using different combinations of gas, liquid and solid for the solvent and solute. All gases are miscible in all proportions. Gases dissolve in liquids and solids. Liquids which are completely soluble in each other in all proportions are said to be completely miscible. Of all inter-phase solutions, it is those between solids and liquids which have received most attention. Generally speaking, non-polar solids dissolve in non-polar solvents and polar solids in polar solvents. In the non-polar fields hydrocarbon, waxes, such as greases, dissolve in hydrocarbon solvents such as chloroform and 1, 1, 1–trichloroethane are used industrially; for this purpose. Polar solvents of which water is the most common example, generally dissolve in polar solids. When a solid is brought into contact with a liquid in which it can dissolve, a certain amount of it passes into solution, until the solution is saturated. In all determinations of solubility it is necessary not only to determine the amount of dissolved substance in solution, but also to ascertain the nature of the solid phase which is in equilibrium with the solution.

Factors that affect solubility. The factors that affect solubility and the rate of solution are :

(*i*) Size of the solute particle. Smaller the size of solute particles faster will be the rate of dissolution.

(*ii*) Rate of stirring of the solution.

(*iii*) Temperature.

Exercise 17.6. *To determine the solubility of potassium chloride from 20°C to 50°C.*

Principle. The solubility of a substance in a liquid at a given temperature is usually defined as the number of grams of the solute required to make a saturated solution in 100 grams of solvent at the given temerature.

Let W_1 grams of solute be dissolved in W_2 grams of solvent, then the solubility per 100 grams of solvent $= \frac{W_1}{W_2} \times 100$ g The direction in which the solubility of asubstance changes with change of temperature depends on the heat of solution. If a substance dissolves at saturation with the evolution of heat the solubility decreases with rise in temperature. On the other hand, if the substance dissolves with absorption of heat the solubility increases with the increase of temperature. The solubility curve is the curve drawn between the solubility and temperature. The solubility curve can take any of the two forms: (*i*) Continuous curve, (*ii*) Discontinuous curve. Fig. 17.4 gives the solubility curves of different solids.

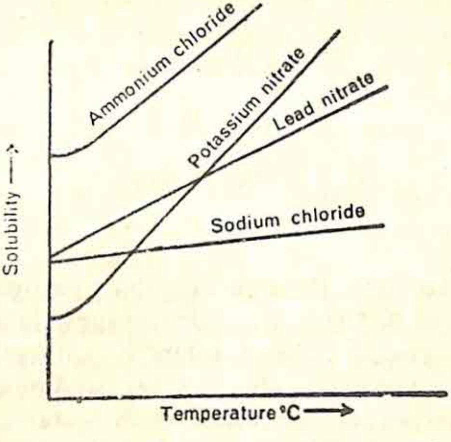


FIG. 17.4. Solubility curves of Different Solids.

Materials required. Thermometer, mechanical stirrer, one ml pipette, china dish, potassium chloride.

Procedure. Prepare a saturated solution of potassium chloride by dissolving an excess of KCl crystals in 100 ml of water at 50°C for 10-15 minutes. Pipette out 5ml of the saturated solution in china dish. The weight of the solution is recorded and it is evaporated to dryness. From the weight of the residue the solubility at 50°C is calculated. Now the solution is allowed to cool to 45 °C and 5ml of the saturated solution is pipetted out, in the china dish. The solution is evaporated to dryness and the weight of the residue gives the solubility at 45°C. This is continued up to a temperature of 20°C. The cooling should preferably be done in a thermostat.

Observations and calculation. Room temperature= °C

Weight of empty china dish $= a$ g

Weight of china dish + solution $= b$ g

Weight of china dish + residue $= c$ g

Weight of residue $W_1 = c - a$

Weight of solvent $W_2 = b - a$

Solubility at......°C $= \frac{W_1}{W_2} \times 100$ g of solute.

The solubility is thus calculated at different temperatures and

Temperature	20°C	25°C	30°C	35°C	40°C	45°C	50°C
solution per 100g of solvent	...	...	...	...	...	...	...

plot a graph of solubility versus temperature.

18

Colloidal State

In an ordinary solution the size of solute particles is generally between $10^{-10}\,m$ and $10^{-9}\,m$. A solution of sugar in water is known as true solution. The particles of solute in true solution cannot be seen by the naked eyes. On the other hand on mixing barium sulphate with water we get suspension which contains particles that are large enough to be seen by the naked eye or under a microscope. Thomas Graham divided soluble substances into two classes, 'Crystalloids' and 'Colloids', according to their powers of diffusion across vegetable or animal membranes. Substances such as sodium chloride, sugar and urea are called Crystalloids and other class includes many amorphous substances like gelatin, starch and gum and were named Colloids (Greek word Kolla=glue and eiods=like). Colloidal state has particles size greater than those of true solution and less than the particle size in a suspension. The particles of colloidal state lie in the range of ($5m\mu$—$200m\mu$) colloids are heterogenous in character and consist of (*a*) Disperse phase, and (*b*) Dispersion medium.

Disperse phase is the phase forming the particles.

Dispersion medium is the medium in which the particles are dispersed. Colloidal solutions are called sol. If the dispersion medium is water they are called hydrosols. Sols are frequently subdivided into lyophobic (solvent hating) and lyophilic (solvent loving) colloids.

Lyophobic colloid. The examples include metal sols, arsenious sulphide sol, and silver halide sol. These are difficult to prepare and easy to coagulate. They need stabilisers for protection and are called irreversible sols.

Lyophilic colloid. The common examples are gelatin, gum arabic, aluminium hydroxide, starches. These are relatively more stable, and are called reversible sols.

Precipitation of colloids. Small amounts of electrolytes are helpful for protecting colloids whereas somewhat larger amounts cause the particles to aggregate and form a visible precipitate. The phenomenon is known as coagulation. Several experiments have been made on the study of precipitating effect, of various electrolytes on different sols.

It has been observed that the ion which is effective in precipitation of sol must have a charge sign, opposite to that of the colloidal particles. Further the precipitation effect increases with the increase in the charge on the ion or the valence of the ion. This statement is known as Schulze-Hardy rules.

Table 18.1 gives the minimum concentrations in millimoles per litre of various electrolytes required to precipitate negatively charged sol, i.e. arsenious sulphide and positively charged sol. i.e., ferric oxide soi.

TABLE 18.1

Minimum electrolyte concentration for precipitation

Arsenious sulphide sol(—ve)			Ferric oxide sol (+ve)		
Electrolyte	*Cation charge*	*Minimum concentration (milimoles)*	*Electrolyte*	*Anion charge*	*Minimum concentration (milimoles)*
NaCl	1	52	KCl	1	103
KNO_3	1	50	KBr	1	137
$1/2K_2SO_4$	1	62	K_2CrO_4	2	0.325
$MgSO_4$	2	08.1	KNO_3	1	131
$BaCl_2$	2	0.69	K_2SO_4	2	0.219
$AuCl_3$	3	0.093	$K_3[Fe(CN)_6]$	3	0.096

Protective colloid. If stable organic colloid such as gelatin is added to a metal sol, the gelatin thus added will prevent the precipitation of the metal sol or the addition of an electrolyte. This is known as protective action and gelatin albumin or gums which exert protective action are known as protective colloids.

Protective power of a protective colloid is expressed in terms of 'Gold number".

Gold number of protective colloid is the number of milligrams of the added colloid which is able to protect 10ml of a red gold sol from coagulation by the rapid addition of 10ml of 10 per cent of common salt solution.

Protective action is a very important phenomenon as it enables collids to be kept.

Exercise 18.1. *To prepare arsenous sulphide sol.*

Principle. Arsenious sulphide is a negatively charged colloid and can be prepared by double decomposition method, i.e. by passing hydrogen sulphide through a dilute solution of arsenious oxide in water, i.e.

$$As_2O_3+3H_2S=\underset{\text{(colloidal sol)}}{As_2S_3}+3H_2O$$

The important precaution in the preparation of colloids is that all the glassware used in the experiment should be thoroughly cleaned and should be free from ionic substances as these would cause coagulation of colloid. This can be done by a method of cleaning called "steaming out".

Procedure. Take 1 litre flask wash it throughly with water and dry by passing steam. A simple experimental arrangement is shown in Fig. 18.1. It consists of a flask fitted with a funnel and a glass tube as shown. The vessel to be cleaned, say a conical flask is placed in the inverted position. Steam is produced by heating the water which passes through the glass tube and cleans the vessel. The condensed water collects in the funnel and is rejected.

Boil 0.5 g finely powdered pure arsenious oxide in 500ml of distilled water in a litre flask for 10 to 15 minutes. Cool the solution and pass a stream of hydrogen sulphide into the solution (until the opalescent liquid becomes turbid and the solution acquires yellowish orange colour). Remove the excess hydrogen sulphide by bubbling a stream of hydrogen through the solution. Filter and collect the filtrate as arenious sulphide sol in a dry conical flask and cork it.

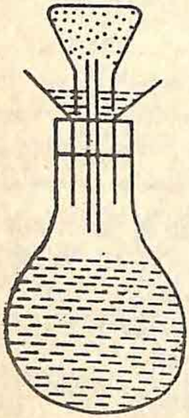


FIG. 18.1

Precautions. (*i*) The apparatus should be thoroughly clean and perfectly dry,

(*ii*) There should be no impurity in the flask.

A brief out line of methods of preparation of some sols are:—

Exercise 18.2. *To prepare sulphur sol.*

Procedure. Add 20ml of 0.1M sodium thiosulphate in 100ml of distilled water. Add dropwise with constant stirring 1ml of dil HCl when sulphur sol is formed.

Exercise 18.3. *To prepare red gold sol.*

Procedure. Add 1ml of 1 per cent gold chloride (chloroauric acid $HAuCl_4$) to about 200ml of distilled water. Make the solution alkaline with 2M-NH_4OH. Add dropwise fresh and dilute tannin solution with stirring until an intense red colour is formed. Heat the solution to boiling and add little more of gold chloride and the tannin solution.

Exercise 18.4. *To prepare ferric hydroxide sol.*

Procedure. Add 20ml of a 2% ferric chloride solution to 200ml of boiling water. Continue to boil the solution and replace the water lost by evaporation till a brown coloured sol is obtained.

Exercise 18.5. *Compare the precipitating power of some electrolytes for precipitating As_2S_3 sol.*

Procedure. Prepare the following solutions.

(*a*) *0.2M NaCl*. Dissolve 11.7g of sodium chloride and make up the volume up to one litre.

(*b*) *0.005M $BaCl_2$*. Dissolve 0.555g of barium chloride and make up the volume up to one litre.

(*c*) *0.0005M $AlCl_3$*. Dissolve 0.688g of aluminium chloride and make up the volume up to one litre. Take ten clean test tubes completely dry them with hot air and lable them from 1 to 10. With the help of a burette add 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5 and 0.0ml of sodium chloride and 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0ml of distilled water in each of them and shake. Now add 5.0ml of arsenious sulphide sol in all the ten test tubes. After each addition cork the test tube and place them in a test tube stand for 15 minutes.

Observe each test tube against dark background and find out the test tube in which the precipitation has just started. The lowest concentration of electrolyte at which the indication for starting of precipitation is obtained gives the precipitation values of the electrolyte. Repeat the experiment for second set of values. Perform similar experiment with barium chloride and aluminium chloride solution as electrolytes determine the minimum concentration of each of these electrolytes record the observations as under.

Observations.

Test tube nos.	*Volume of 0.2M NaCl (ml)*	*Volume of water (ml)*	*Observation*
1.	4.5	0.5	...
2.	4.0	1.0	...
3.	3.5	1.5	...
4.	3.0	2.0	...
5.	2.5	2.5	...
6.	2.0	3.0	...
7.	1.5	3.5	...
8.	1.0	4.0	...
9.	0.5	4.5	...
10.	0.0	5.0	...

Precipitation observed between (*i*)
(*ii*)

Precipitation observed between (*i*)
(*ii*)

Mean precipitation volume of sodium chloride=(say V)

Method of calculation. 0.2M sodium chloride=0.2 millimole per litre.

V ml of NaCl solution=$0.2V$ millimoles

Precipitation value of NaCl is millimoles of electrolyte per litre

$$\text{of solution} = \frac{0.2V}{10} \times 1000$$
$$= 20V$$

Record the observations for $BaCl_2$ and $AlCl_3$ in similar manner and calculate their precipitation values. Compare the results.

Precautions. 1. The apparatus should be clean and perfectly dry.

2. The precipitation stage should be observed by looking vertically down in a tube and compare it with the tube to which no electolyte has been added.

Exercise 18.6. *To study the protective power of a lyophobic sol.*

Principle. Lyophobic sols are inherently unstable in contrast to lyophobic material to a lyophobic sol confer lyophilic properties to it to some extent. This behaviour is known as protective action. One can determine the protective power of different substances i.e. gelatin, gum arabic and starch. Gold number gives the protective power.

Procedure. (*i*) *Preparation of red gold sol.* Add 1ml of 1 per cent chloroauric acid solution to 200ml of water. Make the solution alkaline with 2M NH_4OH. Add dropwise with stirring fresh dilute solution of tannin until an intense red colour is formed. Heat the solution to boiling, add 1ml more of chloroauric acid and little more of tannin solution.

(*ii*) *Determination of protective powers.* (*a*) *Sodium citrate.* Prepare 100ml of approximately 1 per cent (w/v) solution.

(*b*) *Gelatin.* Prepare 0.5 gelatin solution by digesting 1g of gelatin powder in 200ml of water at 40°C to 50°C. Cool the solution.

(*c*) *Starch.* Boil about 1g of soluble starch with 50ml of water for about 5 minutes. Cool the solution and make up quantitatively to 100ml.

(*d*) *Gum arabic.* Dissolve 1g of gum arabic powder in 100ml of water at 50°C. Cool the solution.

(*e*) Prepare 100ml of 10 per cent (w/v) volume.

Take three clean test tubes followed by steam cleaning. In each of them add 10ml of gold sol followed by 0.06, 0.1 and 1.0ml of gelatin solution respectively. Mix well by shaking add 1ml of NaCl solution to each tube. Shake well. View the tubes against a white background, a change of colour from red to purple or to blue, denotes coagulation of the gold sol.

Find out the amount of gelatin that will just prevent the change of colour of red gold sol.

Determine the corresponding values for gum arabic and starch. Record the volume of electrolyte needed for coagulation in each case.

19

Chemical Kinetics

When ice melts to form liquid water or when the liquid water evaporates to gaseous water it involves only a phase change the chemical composition does not change, i.e.,it remains same the chemical compound i.e. water. This is an example of a physical change. On the other hand when a candle burns it forms water and carbon dioxide as the products. These products have many reactions. This is an example of chemical change and a chemical reaction has occurred. We may observe colour changes, gas formation or products with different solubilities as evidence of a chemical reaction. A knowledge of thermodynamic quantities such as heats of reaction, free energies, equilibrium constants etc. enables one to predict the direction of a chemical reaction, but gives no information about the velocity of the reaction. Some reactions are practically instantaneous while other are slow, some reactions occur in presence of a catalyst. A study of the kinetics of a reaction is usually made in order to elucidate the path or mechanism by which it takes place.

A chemical reaction in which energy is released is known as *exothermic reaction.*

A chemical reaction in which energy is absorbed is known as *endothermic reaction.*

How rapidly does a chemical reaction occur is expressed as the rate of a chemical reaction? The study which involves the rate of chemical reactions is known as chemical kinetics. As the reaction proceeds the concentrations of the reactants decreases and those of the products increases and after a certain time their concentrations become constant. This is shown in Fig. 19.1.

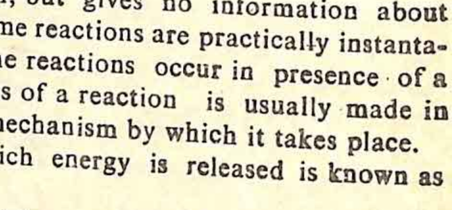


FIG. 19.1

The first step in the empirical study of the kinetics of a reaction is to decide whether it is homogeneous or heterogeneous, catalysed or uncatalysed. The next step is to determine how the rate of reaction depends on the concentration of reactants (and products, if the reaction is reversible).

The velocity of a reaction is expressed as the rate of increase in the molar concentration of a product or the rate of decrease in the concentration of a reaction reactant at some specified temperature.

Consider the general reaction,

$$\text{Reactant} \longrightarrow \text{Products}$$

The rate of a reaction in solution may be measured by measuring the change in concentration of a reactant per unit time.

Let C_1 be the concentration of the reactant of time t_1 and C_2 at any other time t_2.

$C_1 - C_2$ is the change in concentration that has occurred in the time $t_2 - t_1$. Therefore rate is approximately given by

$$\left(\frac{C_1 - C_2}{t_2 - t_1}\right)$$

However, this is not the actual rate, because this applies the time interval $t_2 - t_1$ and not at the particular instant of time t_1.

$$\text{Rate} = \lim_{\Delta t \to 0} \left(\frac{C_1 - C_2}{t_2 - t_1}\right)$$

$$= \lim_{\Delta t \to 0} \left(-\frac{\Delta C}{\Delta t}\right)$$

$$\therefore \quad \text{Rate} = \frac{-dc}{dt}$$

or

$$-\frac{dc}{dt} = kc^n$$

where k is a constant called the reaction rate constant or specific reaction rate and n is the order of a reaction. The order of a reaction may be defined as the number of atoms or molecules whose concentrations or pressures determine the order of a reaction.

First Order Reactions. The reaction is said to be of first order in which the rate of a reaction is proportional to the first power of the concentration of any one of the reacting substance. Consider a first order reaction of the type

$$A \longrightarrow \text{products} \qquad \ldots (19.1)$$

The rate is directly proportional to the concentration of the reacting substance, i.e.,

$$-\frac{dc}{dt} = kc^n \qquad \ldots (19\ 2)$$

or

$$nc = -kt + B \qquad \ldots (19.3)$$

where B is the integration constant. If a is the initial concentration, and x is the decrease in concentration after time, t

then $c=(a-x)$

$\therefore$ Equation (19.3) can be written as

$$\frac{dx}{dt}=k(a-x)$$

This integration and rearrangement gives us

$$2.303 \log a-2.303 \log (a-x)=kt \qquad \ldots (19.4)$$

For a first order reaction a plot of $\log (a-x)$ against t is linear and slope of $-k/2.303$ and the rate constant can thus be calculated. It follows from the first order rate equation that the value of the velocity constant k is independent of the concentration units chosen and depends only on the time units chosen.

Examples of first order reactions. For example the decomposition of nitrogen pentoxide is a first order reaction

$$N_2O_5\ (g) \longrightarrow N_2O_4\ (g)+\tfrac{1}{2}O_2\ (g)$$

The rate of decomposition reaction is proportional to the concentration of nitrogen pentoxide.

The hydrolysis of ethyl acetate in aqueous solution in the presence of a mineral acid proceeds as under. The reaction is catalysed by mineral acid. The water is present in such a large concentration that its concentration remains unchanged. The reaction can be followed by estimating the amount of acetic acid by titrating it with sodium hydroxide.

$$CH_3COOC_2H_5+H_2O \longrightarrow CH_3COOH+C_2H_5OH$$

Hydrolysis or Inversion of cane sugar. Inversion of cane sugar proceeds in presence of acids as,

$$C_{12}H_{22}O_{11}+H_2O=\underset{\text{glucose}}{C_6H_{12}O_6}+\underset{\text{fructose}}{C_6H_{12}O_6}$$

The course of the reaction can be followed by measuring the angle of rotation of plane polarised light in a polarimeter.

Many chemical reactions are not kinetically simple. They proceed through a number of steps between initial reactants and final products. Molecularity of reaction is the number of atoms, ions or molecules taking part in each step leading to a chemical reaction. Reaction which proceeds in two or more steps molecularity is assigned to each step.

When the molecularity of a reaction is one it is known as unimolecular reaction. For reactions having molecularity two are known as bimolecular reactions.

Second Order Reactions. Most reactions occur by bimolecular processes and many reactions in solution follow second order kinetics. When the rate of a reaction as determined in the laboratory is proportional to the concentration of each of the two reacting substances, the reaction is of second order. Consider the reaction.

$$A+B \rightleftharpoons AB$$

Let a and b represent the initial molar concentrations of two reacting substances A & B, and if x denotes the number of moles per litre which react in interval of time t, then the velocity of the reaction is expressed by the equation,

$$\frac{dx}{dt}=k\,(a-x)(b-x) \qquad \ldots (19.5)$$

On integrating equation (19.5) and evaluating the value of the integration constant, we get

$$k=\frac{2.303}{t(a-b)}\ \log\ \frac{b(a-x)}{a(b-x)} \qquad \ldots (19.6)$$

When A and B present in equal concentrations, i.e., $a=b$ we get from (19.5)

$$\frac{dx}{dt}=k(a-x)^2 \qquad \ldots (19.7)$$

On integrating this we get,

$$k=\ \frac{x}{ta(a-x)} \qquad \ldots (19.8)$$

The value of k in the second order reaction depends on the units in which the concentration is expressed, since the magnitude of $(a-b)$ depends on the units used. The constant k has the dimensions litres $\text{mole}^{-1}\ \text{sec}^{-1}$.

Exercise 19.1. *To study the hydrolysis of methyl acetate in presence of hydrochloric acid.*

Principle. Esters get hydrolysed in aqueous solution, though the reaction proceeds very slowly its rate can be enhanced in presence of strong acid like hydrochloric acid. It can be followed by volumetric estimation of the acetic acid formed, according to the reaction.

$$CH_3COOCH_3+H_2O \overset{H^+}{\rightleftharpoons} CH_3COOH+CH_3OH$$

This is an example of pseudo unimolecular reaction. This is because the concentration of water is high and practically remains constant during the reaction. The object of the experiment is to show that the process is first order with respect to methyl acetate. The order with respect to the ester may be found using a dilute solution in aqueous acid, since the concentration of hydrogen ions, the actual catalyst, remains practically constant throughout the reaction. If aliquots of the solution are removed throughout the reaction. If the aliquots of the solutions are removed at various times and titrated with standard sodium hydroxide, then the first order kinetic equation becomes

$$k=\frac{2.303}{t}\log\left(\frac{V_\infty-V_o}{V_\infty-V_t}\right)$$

where k is a rate constant of the reaction, V_o, V_t and V_∞ are the titres at the beginning of the reaction, after a time t, and at the end of the reaction, respectively.

Procedure. Take 100ml HCl in a 250ml stoppered flask in water tub and also place a stoppered tube containing 20ml of methyl acetate in the same tub. After 10-15 minutes pipette exactly 5ml of methyl acetate in a flask of acid and note the time. Shake thoroughly and immediately withdraw 5ml of the reaction mixture and pour it in about 25ml of ice cold water to arrest the reaction. Note the time to the nearest 15 per cent at which the pipette has been half discharged into the water of the titration flask. Titrate the solution quickly with 0.05N NaOH using phenolphthalein indicator and calculate the volume of alkali required for titration. Let V_o be the volume of alkali used for titration. This will correspond to the concentration of HCl in the reaction mixture before the hydrolysis starts. Pipette out 2ml of reaction at successive intervals of 10, 20, 30, 40, and 50 minutes and transfer them to the flask containing 25ml of ice cold water and titrate them with sodium hydroxide. Note down the volume of alkali V_t, used in each titration.

For determining V_∞, take out 10ml of the reaction mixture in a dry conical flask and loosely cork it. Keep this in a water bath and heat it for about half an hour when the hydrolysis is complete. Pipette out 2ml of the reaction mixture titrate with 0.05N–NaOH. The volume of NaOH used in the titration gives the value of V_∞ The observations are recorded in Table 19.1

Observations. Temperature of bath = ...°C

TABLE 19.1

Time in minutes (t)	*Titre value* V_t	$V_\infty-V_t$	$k=\frac{2.303}{t}\log\frac{V_\infty-V_o}{V_\infty-V_t}$
0	V_o	...	...
10	...	...	...
20	...	...	...
30	...	...	...
40	...	...	...
50	...	...	...
∞	V_∞	...	...

(*i*) The values of k are calculated using the formula

$$k=\frac{2.303}{t}\log\left(\frac{V_\infty-V_o}{V_\infty-V_t}\right)$$

which should come out to be constant within experimental errors.

(*ii*) Plot a graph between of t versus $(V_\infty-V_t)$

Exercise 19.2: *To determine the rate constant of the hydrolysis of ethyl acetate by sodium hydroxide.*

Theory. The hydrolysis of ethyl acetate with sodium hydroxide is a bimolecular and second order reaction, that proceeds according to the following chemical equation:

$$CH_3COOC_2H_5+Na^++OH^-=CH_3COO^-+Na^++C_2H_5OH$$

The reacting species are ethyl acetate and the hydroxyl ion. As the reaction proceeds, each hydroxyl ion, removed in the formation of ethanol, removes one molecule of ethyl acetate, x being the number of mol dm^{-3} of either OH^- or ethyl acetate so removed. The value of x at any time t can be determined by substracting the concentration of sodium hydroxide at time t from the initial value, a. The concentration of sodium hydroxide is determined by back titration with alkali after the addition of excess of hydrochloric acid using phenolphthalein indicator.

The reaction rate will be given by:

$$\frac{dx}{dt}=k[(CH_3COOC_2H_5)][(NaOH)]$$

$$k=\frac{x}{t\ a\ (a-x)}$$

where a is the initial concentration of the ester and $(a-x)$ is the amount of the ester remaining after time t, k is the rate contant.

Procedure. Take 2ml of ethyl acetate and make up a total volume of 100ml with distilled water. Take 100ml of $\frac{M}{40}$ NaOH in separate dry 250ml conical flask. Cork and place them in a trough of water for 5-10 minutes till the two solutions attain a constant temperature. Pipette 50ml of ethyl acetate in a 250ml conical flask and to this add 50ml of NaOH. Start the stop watch, when half the volume of alkali has been added. Take eight 100ml conical flasks each containing 25ml of ice cold $\frac{M}{40}$ HCl. Pipette out 10ml of the reaction mixture after 4, 10, 15, 20, 30, 40, 60 and 100 minutes into each of these flasks. The ice cold HCl helps to arrest the reaction. Titrate each of these reaction mixture with $\frac{M}{40}$ NaOH.

Record the volumes of NaOH required for the back titration of excess of acid, and the temperature of water trough.

Observations. The observations are recorded in a manner shown in Table 19.2

TABLE 19.2

Time Min.	*Titre value of $\frac{M}{40}$ NaOH*	*Volume of $\frac{M}{40}$* NaOH equivalent to unreacted NaOH in the reaction mixture, V_2	$a-x$ $=\frac{V_1-V_2}{25}\times 1000$	$\frac{1}{a-x}$ *vs t*	*k from the graph*

Method of Calculations. From the observations recorded in Table 19.2 it is possible to calculate the value of k which will turn out to be constant for all observations. One can also plot a graph between. $\frac{1}{a-x}$ *vs t* and calculate the value of k.

Exercise 19.3 – *To study the kinetic of the reaction between potassium persulphate* ($K_2S_2O_8$) *with potassium iodide by Clock method.*

Theory : The reaction of potassium persulphate with a solution of potassium iodide containing starch and a low concentration of sodium thiosulphate. The persulphate ions oxidise iodide ions to iodine in preference to oxidising thiosulphate ions

$$2\,I^- + S_2O_8^{2-} \rightarrow 2\,SG_4^{2-} + I_2 \text{ (slow)}$$

However the liberated iodine can not colour starch blue as it reacts instantaneously with the thiosulphate ions

$$I_2 + S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\,I^- \text{ (fast)}$$

This continues till the whole of thiosulphate has been consumed and then the solution becomes blue. The blue colour of the solution is due to the formation of starch-iodide complex. At given concentration and temperature this reaction has been found to have clock-like accuracy. This is why the reaction is called clock-reaction. The reaction can be monitored by sodium thiosulphate solution.

Procedure : Take 250 ml of 0·01 M potassium persulphate solution ($K_2S_2O_8$) in 400 ml beaker. In another beaker take 250 ml solution containing 0·3 M K I + 0·0005 M sodium thiosulphate +

starch. Keep the solutions in a trough of water till their temperature becomes constant. Label these solutions as solution A and solution B.

Take two 100 ml beakers—in one beaker take 25 ml of solution A and in other beaker take 25 ml of solution B. Mix the two solutions and start the stop watch. Note the time when the blue color first appears. Repeat the mixing of solutions and note down the time of appearance of blue color. The experiment is repeated by changing the concentration of potassium persulphate and keeping the solution B, 25 ml in each case.

Solution A	25 ml	20 ml	15 ml	10 ml
Water	0	5 ml	10 ml	15 ml
Total volume	25 ml	25 ml	25 ml	25 ml

Calculate the order of the reaction with respect to potassium persulphate.

20

Conductometric Titrations

20.1 INTRODUCTION

When a metallic conductor forms part of an electrical circuit, it opposes a certain resistance to the passage of the current. The resistance depends on the material of the conductor, on its length, and on its cross-section. The resistance offered by a cube of a material having a side 1cm is called the specific resistance or resistivity of the material. The reciprocal of resistance, 1/R is generally called conductance or conductivity, i.e.,

$$L = \frac{1}{R} \qquad \ldots (20.1)$$

Since,

$$R = \rho\left(\frac{l}{a}\right) \qquad \ldots (20.2)$$

conductance is measured in ohm^{-1} or mho.

The reciprocal of specific resistance (ρ) is called specific conductance *k* (kappa), i.e.,

$$k = \frac{1}{\rho} = \left(\frac{l}{a}\right)\frac{1}{R} \qquad \ldots (20.3)$$

Units of *k* are ohm^{-1} cm^{-1} or *mho* cm^{-1}.

Specific conductance of a solution may be defined as the conductance of a solution placed between electrodes 1 cm^2 in area and 1 cm apart. In comparing the conducting properties of different substances, one should compare chemically comparable quantities of substances, e.g., equivalent or equi-molar quantities. This is known as equivalent conductance (Λ) i.e.

$$\Lambda = \left(\frac{l}{a}\right)\frac{1}{R} \times \frac{1000}{C} \qquad \ldots (20.4)$$

where *C* is the number of equivalents of the electrolyte. The units of equivalent conductance are ohm^{-1} cm^2 $equiv^{-1}$.

20.2 EXPERIMENTAL DETERMINATION OF CONDUCTANCE

For determining the conductance of a solution, one measures the resistance of a solution, using wheatstone bridge circuit (Fig 20.1). Since during the electrolysis of an aqueous solution between platinum electrodes gases are evolved which results in the production of back electromotive force or polarisation. This can be minimised by using alternating current of strength 1000-2000 cps. The electrodes of the conductivity cell are coated with platinum black. The typical conductivity cell employed is shown in Fig 20.2.

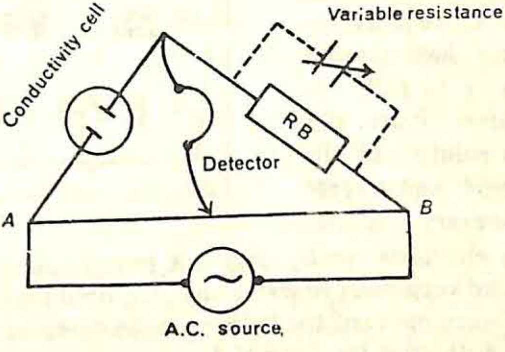


FIG. 20.1. Conductivity Bridge.

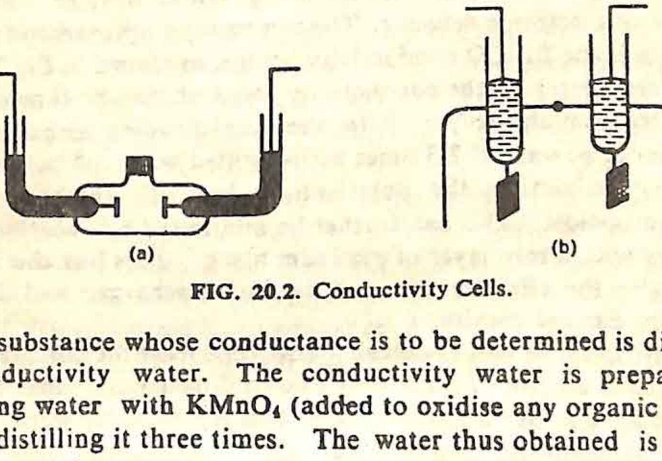


FIG. 20.2. Conductivity Cells.

The substance whose conductance is to be determined is dissolved in conductivity water. The conductivity water is prepared by distilling water with $KMnO_4$ (added to oxidise any organic matter) and redistilling it three times. The water thus obtained is known as conductivity water.

Platinising the electrodes. Clean the platinum electrodes with a warm solution of dichromate and concentrated sulphuric acid. Wash it with distilled water until free from acid. Place some quantity of the platinising solution. The platinising solution can be obtained by dissolving 3g of chloroplatinic acid, 0.025g of lead acetate per 100ml water. The electrodes are connected to a battery of 4 volts and current is so adjusted that there is only a moderately rapid evolution of hydrogen. The current is reversed after every half minute and electrolysis is carried for about 5 minutes. Place the electrodes in a solution of dilute sulphuric acid and reverse the current after every one minute. Wash the electrodes with distilled water and keep them in water until required for use. The null point or the balance point of the bridge can be detected using headphones. At the null point the potentials across the pointer are equal. Initially the movable contact is kept near the centre of the ratio-arm wire AB and the resistances are plugged out from the resistance box such that the loudness of the note in the headphone is reduced to a minimum value. The loudness can further be minimised by adjusting the position of the pointer. Alternatively the accurate position of null point can also be determined using visual devices such as magic eye or electronic detector. The commonly employed conductivity bridge is the ELICO conductivity bridge, as shown in Fig 20.3.

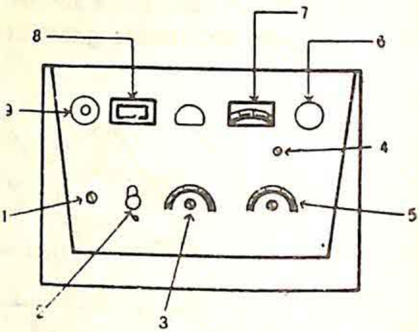


FIG. 20.3. ELICO Conductivity Bridge.

All glass vessels in the conductivity work should be thoroughly washed free from electrolyte After the usual cleaning with chromic acid it should be washed 2-3 times with distilled water. The use of a.c. greatly minimises the polarisation, but still there will be some polarisation. This can further be minimised by coating the electrodes with a thin layer of platinum black. This has the effect of increasing the effective area of current discharge, and hence reduces the current density.

Determination of cell constant. The cells used for conductivity measurements are not of accurately known dimensions, and therefore these have to be calibrated before use, for accurate work.

The calibration of conductivity cells is generally done with solutions of potassium chloride at a temperature of 25°C. A quantity of pure KCl is weighed out and the requisite quantity of water is added to produce exactly 0.1 or 0.01 demal solution. (Demal solution can be prepared by dissolving 1 gram equivalent per 1000g of solution). This solution is taken in the conductivity cell and its resistance is determined. The specific conductivity of KCl can be taken from the Table 20.1 and the cell constant is thus calculated.

TABLE 20.1

Specific Conductivity of KCl solution.

Temperature °C	*Conductivity of KCl* *0.1 demal*	*0.01 demal*
0	0 007138	0.0007736
18	0.011167	0.0012205
25	0.012856	0.0014088

20.3 CONDUCTOMETRIC TITRATIONS

When the solution of one electrolyte is added to another a change in conductance will result on account of volume changes and possible ionic reactions which occur in the solution. Consider an electrolyte (A^+B^-) which is added to another electrolyte (C^+D^-), if the addition is done in such a manner that there is no appreciable volume change and there is no chemical reaction, the conductance of CD gradually increases on the addition of AB. The chemical reaction can be symbolised as under:

$$A^+B^- + C^+D^- \longrightarrow A^+D^- + CB$$

in which the product CB is either only slightly ionised or is insoluble, then a marked change of conductance occurs at the equivalence point. During the titration A^+ replaces C^+ and the conductance may increase or decrease depending on the relative mobility values of A^+ and C^+.

The addition of an alkali to a strong acid is accompanied by a decrease in conductance due to the replacement of H^+ by the less mobile cation. When the neutralisation is complete, i.e.,all the hydrogen ions have been removed. Any further addition of base results in an increase in conductance due to the presence of excess of OH^- ions. The different types of conductivity titration curves are given in Fig 20.4.

Exercise 20.1. *To determine the strength of given HCl (0.01N) by titrating against sodium hydroxide (0.1N) conductometrically.*

Material required. Conductivity bridge, conductivity cell; 0.1N NaOH.

Procedure. Pipette out 20ml of given hydrochloric acid in a 100ml beaker. Keep the cell dipped in acid. Make the connections of the conductivity bridge. Record the temperature of the solution and measure the resistance of the solution. Add small portion of

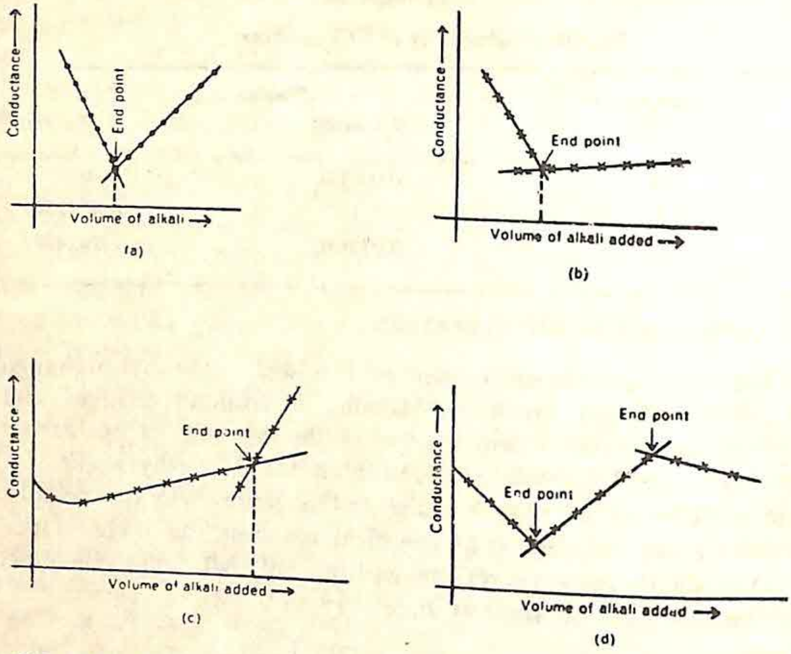


FIG. 20.4. Types of coductivity titration curves (*a*) strong acid *vs* strong base, (*b*) strong acid *vs* weak base, (*c*) weak acid *vs* strong base (*d*) mixture strong acid and weak acid *vs* strong base.

alkali (~0.2ml) from the burette. Stir the solution and measure the resistance of the solution. Continue the addition of alkali and measure the resistance of the solution after each addition. Take at least five, six readings beyond the equivalence point.

Observations and Calculations. Room temperature = °C

Sl.No.	*Volume of NaOH added* (ml)	*Observed resistance* (ohms)	*Conductance* $L = \frac{1}{R}$
1.	...	...	...
2.	...	...	...
3.	...	...	...
4.	...	...	...
5.	...	...	...

Plot a graph of conductance against the volume of titrant added. Apply the volume correction.

Exercise 20.2. *To determine the strength of given acetic acid ($\simeq$ 0.01N) by titrating against sodium hydroxide (0.1N).*

Procedure. Pipette out 20ml of given acetic acid in a 100ml beaker and titrate against NaOH (0.1N) in the same manner as explained in Exercise 20.1. Plot a graph of volume of titrant against the conductance of the solution and calculate the strength of the given acetic acid.

Exercise 20.3. *To determine the strength of a mixture of HCl and acetic acid conductometrically.*

Procedure. Pipette out 20ml of mixture of acids in a conductivity cell and titrate in the similar manner as explained in Exercise 20.1. Plot a graph of conductance against the volume of titrant added. In this case we get two equivalence points. The first is due to the neutralisation of strong acid and second one is due to the neutralisation of the weak acid. The first end point (inflexion) gives the volume of alkali used for strong acid and the second inflexion gives the volume used for the titration of the weak acid.

It is also possible to carry out precipitation titration conductometrically (i.e., the titration of KCl or NaCl against $AgNO_3$ solution).

21

Potentiometric Measurements

21.1 INTRODUCTION

Voltaic cells are very useful in physical chemistry as they provide a convenient means, of measuring directly the free energy change in chemical reactions. When a voltaic cell is discharged, the free energy of the cell reaction becomes available for performing useful work. Redox reactions have been used for a longtime as source of energy. More recently, they have been used in fuel cells. The energy produced is electrical energy which can be measured very precisely. Let us consider a familiar redox reaction between zinc and a copper sulphate solution

$$Z_n(s)+C_u^{2+}(aq)\rightleftharpoons Z_n^{2+}(aq)+C_u(s)$$

The reaction can be considered to proceed in two steps. The zinc ion donates two electrons:

$$Z_n(s)\rightarrow Z_n^{2+}(aq)+2e^-$$

The copper ion accepts two electrons

$$C_u^{2+}\ (aq)+2e^- \longrightarrow C_u(s)$$

The zinc goes from 0 to +2 oxidation state where as copper from +2 to 0. The reaction can be brought about by simply mixing zinc dust with copper sulphate solution. A cell with zinc and copper electrodes is shown in Fig 21.1.

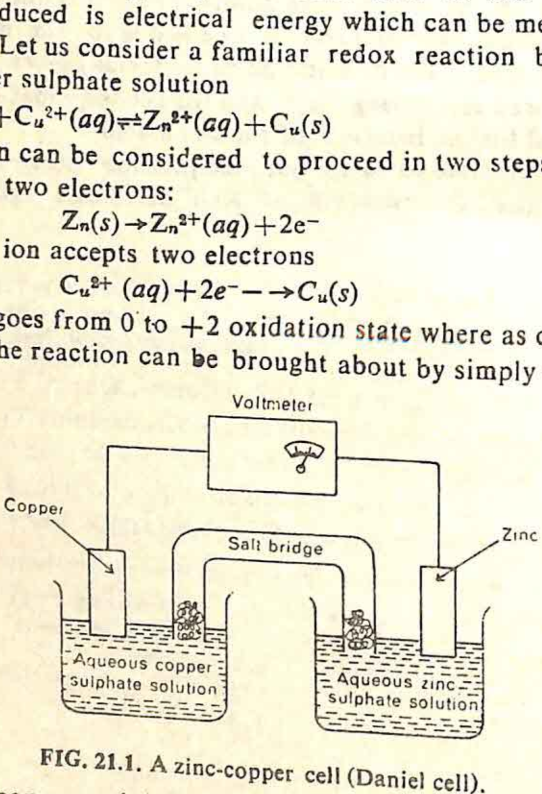

Voltmeter
Copper
Salt bridge
Zinc
Aqueous copper sulphate solution
Aqueous zinc sulphate solution

FIG. 21.1. A zinc-copper cell (Daniel cell).

If the cell is short circuited the reaction will proceed until an equilibrium is reached, in this case well over to the right hand side of the equation. The solution will get hot producing the same amount of heat, equal to as in the case of direct mixing. All the energy from the reaction can be released as thermal energy within the system. To get the maximum amount of electrical energy from the cell it will be necessary to have the highest voltage, therefore, the smallest current, which in other words means that the energy will have to be taken out, very slowly. The maximum work that can be theoretically obtained from the cell is given by

$$W_{max} = n \times E \times F \qquad \ldots(21.1)$$

where n is the number of moles of electrons, F is faraday constant and E is the electromotive force.

The free energy change (ΔG) of the process is given by

$$\Delta G = -nEF \qquad \ldots(21.2)$$

21.2 ELECTRODE POTENTIALS

Consider a copper rod dipping in a solution of copper sulphate. There is a tendency of the metal ion to pass into solution, in the form of +ve ions. This property of the metal is known, as its solution, pressure. This tendency of the metal to pass into solution as ions, is opposed by the reversed tendency of the ions to get deposited back on to the electrode. This is due to the osmotic pressure of the ions in solution. The standard electrode potential of the metal is equal to the difference between its solution pressure and the osmotic pressure of its ions.

Now the problem is, how to measure the electrode potential. Unfortunately a single electrode potential can never be measured directly. However, it can be measured indirectly by coupling the electrode whose single electrode potential is measured with a reference electrode.

There are two types of reference electrodes:

(*a*) Primary reference electrode.
  (*i*) Hydrogen electrode.
(*b*) Secondary reference electrodes.
  (*i*) Calomel electrode,
  (*ii*) Glass electrode,
  (*iii*) Quinhydrone electrode.

Hydrogen electrode. This is a primary reference electrode. A typical hydrogen electrode is shown in Fig. 21.2.

A normal hydrogen electrode can be set up by bubbling in pure hydrogen gas at a pressure of one atmosphere through a solution of an acid in which the activity of hydrogen ions is unity. A platinised platinum plate is used as electrode. By convention the e.m.f of this electrode is assigned a value 0.0 volt.

In hydrogen electrode, platinum is poisoned by the adsorbed impurities from the solution. It can be constructed only when there is a pure hydrogen gas generator.

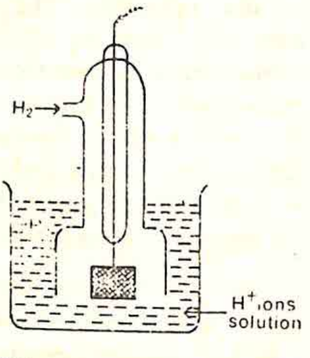


FIG. 21.2. Hydrogen Electrode.

Calomel electrode. It is a convenient secondary reference electrode and consists of mercury in contact with a solution of potassium chloride saturated with mercurous chloride.

First prepare 1N solution of KCl from pure and dry sample. The electrode vessel is washed with chromic acid, water and finally with distilled water. It is then dried and 1-2ml of pure mercury is added at the bottom of the vessel. Over this a thin layer of calomel paste (prepared by rubbing together in a mortar, calomel, mercury and potassium chloride) is poured. It is then washed two or three times with a minimum quantity of potassium chloride. The vessel is then filled with the solution of potassium chloride.

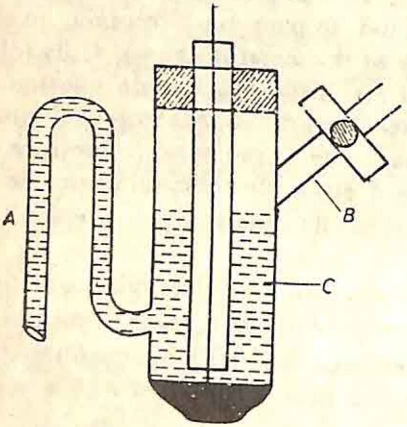


FIG 21.3. Calomel Electrode.

The e.m.f. of calomel electrode is expressed with reference to the normality of KCl solution.

For 0.1N-KCl,$E^\circ = 0.3345$ volt.

A typical calomel electrode is shown in Fig. 21.3.

Quinhydrone electrode. Billmann introduced the use of quinhydrone electrode for the determination of pH. This is a redox electrode at which the reversible reaction occurs. The quinhydrone electrode has a gold wire dipped in a solution of unknown pH. The solution is made saturated with quinhydrone. The quinhydrone electrode is extremely simple to set up and gives its true reversible potential. It is applicable to many types of solutions and gives pH values as accurately as the hydrogen electrode.

Salt bridge. When both electrodes of a cell have the same electrolyte solution it is immaterial how the halves are connected; the two electrodes may be either in the same vessel or in separate compartments which are joined with a salt bridge, to minimise the liquid junction potential. The salt bridge usually consists of a saturated solution of KCl. A suitable jelly is prepared by dissolving about 3g of KCl and 0.3g of agar powder in 10ml of water. The contents are heated in a small beaker on a steam bath when a clear solution is obtained. It is sucked while hot into U tubes and is cooled under a tap of water, when the mixture sets to a gel. Agar gels with KNO_3 or NH_4NO_3 can also be used where necessary.

For an electrode of metal M, which shows following equilibrium:

$$M^{n+} + ne \rightleftharpoons M$$

The e.m.f. of the electrode is given according to Nernst Equation

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Reduced}]}{[\text{Oxidised}]} \qquad \ldots(21.3)$$

where n stands for the number of electrons involved in the electrode reaction, F is faraday and has a value of 96,500 coulombs. $R = 8.314$ joules mole^{-1} deg^{-1}, $T = 298$K.

Galvanic cells are made by arranging for a spontaneously occurring oxidation-reduction reaction to proceed in such a way that electrons are transferred from the reducing agent to the oxidising agent by means of an external circuit.

Exercise 21.1. *To set up a galvanic cell and to measure its emf.*

Materials required. Copper and zinc rods, connecting wires, glass tube sealing wax, 1M copper sulphate,1M zinc sulphate solution, dilute sulphuric acid, dilute nitric acid, mercury and a saturated calomel electrode.

Procedure. Take zinc and copper rods of 5-6cm in length. Solder insulated connecting wires to each one of these. Amalgamate the zinc rod by rubbing mercury over it in presence of dilute sulphuric acid. Wash the rod with water and dry with filter paper.

Dip the copper rod after cleaning with cloth in dilute nitric acid. Deposit a thin layer of copper electrolytically. Take two beakers each of 100ml capacity, fill one of these with 0.1 M $ZnSO_4$ solution and the other one with 0.01M copper sulphate solutions. Place a KCl salt bridge and connect the two solutions. Put the copper rod in copper sulphate solution and zinc rod in the solution of zinc sulphate.

The e.m.f. of the cell is measured with the help of a potentiometer. The experimental arrangement is shown in Fig 21.4.

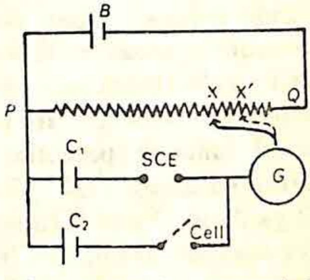


FIG. 21.4. Measurement of the cell e.m.f.

The method is based on the comparing the e.m.f. of the given cell against a standard cell (SCE). First the saturated calomel electrode (SCE) is put in the circuit and balance the circuit by moving the deflection in the galvanometer to X. Now place the given cell in the circuit through the key and locate the balance point X′.

Observations.

Room temperature= °C

Sl. No.	*Given cell PX′* (Cm)	*Standard cell PX* (Cm)
1.	...	...
2.	...	...
3.	...	...

Calculation.

$$\frac{E_{\text{cell}}}{E_s} = \frac{PX'}{PX}$$

or

$$E_{\text{cell}} = E_s \cdot \frac{PX'}{PX}$$

where E_s is the e.m.f. of the standard cell (SCE). The e.m.f. of the cell E_{cell} can thus be calculated.

Result. The e.m.f. of the given cell was found to be. . . . . volts.

21.3 POTENTIOMETRIC TITRATIONS

Potentiometric titrations are amongst the most accurate known because the potential follows the actual change in concentrations. and therefore, the end point will often coincide directly with the equivalence point. In potentiometric titrations, interest is focussed upon the changes in e.m.f. of an electrolytic cell as a titrant of a precisely known concentration is added. Since, the potential of an electrode dipping in a solution of an electrolyte depends on the concentration of the ions with which it is in equilibrium. It is this potential change which is used as an 'indicator' in volumetric analysis.

On adding small amount of a standard solution of alkali to the acid, the e.m.f. of the cell will slightly change. This is because the change in electrode potential depends on the fraction of hydrogen ions removed by each drop of alkali solution. As the amount of alkali added approaches equivalence to the amount of hydrogen ions there will be a sharp increase in the e.m.f. as the equivalence point is passed, there will again be a slow change. On plotting the e.m.f. against volume, the shape of the curve obtained is shown in Fig. 21.5.

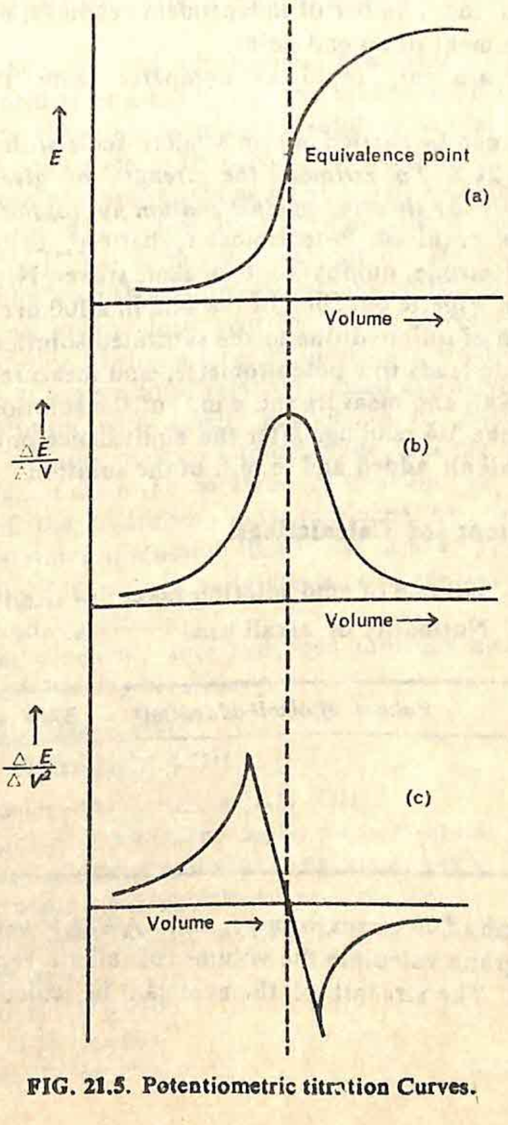


FIG. 21.5. Potentiometric titration Curves.

The end point of the titration is given by the point of inflexion of the curve. The point of inflexion can also be obtained by plotting the values of $\triangle E/\triangle V$ against volume, the point of inflexion will corres-pond to the value where $\triangle E/\triangle V$ is maximum. Alternatively a plot of $\Delta^2 E/\Delta V^2$ against volume will also give the equivalence point. This is shown in Fig.21.5.

There are numerous advantages of the potentiometric method of titration. Some of them are:

(*i*) potentiometric titrations are very reliable since the result depends on the number of independent readings, not on one subjective judgement of an end point.

(*ii*) these are very rapid as compared with the gravimetric methods.

(*iii*) these can be carried out on a micro-scale with little difficulty.

Exercise 21.2. *To estimate the strength of given hydrochloric acid (≃0 01N) by titrating against sodium hydroxide.*

Materials required. Potentiometer, battery, calomel electrode, platinum electrode, quinhydrone, beaker, stirrer, N/10 NaOH.

Procedure. Pipette out 20ml of the acid in a 100ml capacity beaker. Add a pinch of quinhydrone to the saturated solution. Connect the two electrode leads to a potenitometer, and measure the e.m.f. Add 0.5ml of alkali and measure the e.m.f. of the solution. Continue the addition, take 3-4 readings after the equivalence point. Record the volume of alkali added and e.m.f. of the solution.

Observations and Calculations.

Volume of acid solution taken = ...ml
Normality of alkali used =

Sl. No.	*Volume of alkali added (ml)*	*EMF of the cell (Volts)*
1.	...	...
2.	...	...
3.	...	...
		...

Plot a graph of E versus volume, and $\Delta E/\Delta V$ versus volume and from the graph calculate the volume of alkali required for neutralisation. The strength of the acid can be calculated using the relation..

$$N_1V_1 = N_2V_2$$

where N_1 = normality of the acid.

V_1 = volume of the acid taken.

N_2 = normality of the alkali.

V_2 = volume of the alkali used (calculated from the graph).

Result. The strength of the given acid was found to be . . . . g/l.

21.4 MEASUREMENT OF HYDROGEN ION CONCENTRATIONS

Most of the chemical and biochemical processes are profoundly affected by the acidity or alkalinity of the media in which they take place. All acids dissociate in aqueous solution to yield hydrogen ions. Now add acids such as HCl, H_2SO_4 and HNO_3 are completely ionised in aqueous solution where as CH_3COOH, HCOOH ionise to a small extent only. The former are known as 'strong' acids and the later as 'weak'. If we compare solutions of 1N HCl and 1N, CH_3COOH we find even though the molar concentrations of the two acids are the same, hydrochloric acid ionises extensively and yields a strong acid solution having a large proportion of hydrogen ions.

Acetic acid as it ionises to a relatively small extent yields only a weakly acid solution with small proportion of hydrogen ions. These observations do make us to conclude that the acidity of a solution depends not upon the molarity of the acid but upon the concentration of the hydrogen ions, produced by the acid. It follows from the above discussion that if we know hydrogen ion concentration $[H^+]$ for a given solution we can express the acidity of that solution quantitatively.

Water is weakly ionised into hydrogen ions and hydroxyl ions according to the following reaction,

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

The ionic product of water $K_w = [H^+]\ [OH^-]$

It means that the product of the molar concentrations of H^+ and OH^- ions in dilute solutions is always the same at any given temperature no matter what other substances may be present. For pure water $[H^+] = [OH^-] = 10^{-7}$. In terms of hydrogen ion concentrations we can define the terms,

neutral if $[H^+] = 10^{-7}$
acidic if $[H^+] > 10^{-7}$
alkaline if $[H^+] < 10^{-7}$

The hydrogen ion concentration can be measured accurately using suitable methods. The acidic and alkaline nautre of a solution can be expressed in terms of hydrogen ion concentration. Due to some practical difficulties, the acidity or alkalinity of a solution is not expressed in terms of hydrogen ion concentration. Sorensen suggested the use of pH (puissance d'hydrogen) scale. On this scale pH of any solution is defined as:

$$pH = -\log_{10} a_{H^+} \qquad \ldots (21.4)$$

where a_{H^+} is the activity of the hydrogen ions. For dilute solutions activity can be replaced by concentration, i.e.,

$$pH = -\log_{10}[H^+] \qquad \ldots (21.5)$$

pH scale is a logarithmic. The *p*H of a solution is defined as the negative logarithm of the hydrogen ion concentration. The pH scale has values between 0 and 14 as shown below:

H^+ 10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

acid neutral alkaline

FIG. 21.6. *p*H scale.

The *p*H of a solution can be accurately measured with the help of a *p*H meter. However the approximate value of *p*H can also be determined using a multiple range indicator solution. These are known as universal indicators. One such indicator is prepared by dissolving 0.1g of phenolphthalein, 0.2 g of methyl red 0.3 g of

TABLE 21.1

Acid-base Indicators

Indicator	*Acid colour*	*Base colour*	*pH range*	
Thymol blue	red	yellow	1.2-2.8	1.7
Methyl yellow	red	yellow	2.9-4.0	3.3
Bromophenol blue	yellow	blue	3.0-4.6	4.1
Methyl orange	red	yellow	3.1-4.4	3.7
Bromocresol green	yellow	blue	4.0-5.6	4.7
Methyl red	red	yellow	4.2-6.3	5.0
Bromocresol purple	yellow	purple	5.2-6.8	6.1
Bromothymol blue	yellow	blue	6.0-7.6	7.1
Phenol red	yellow	red	6.8-8.4	7.8
Thymol blue	yellow	blue	8.0-9.6	8.9
Phenolphthalein	colourless	red	8.3-10.0	9.7
Thymolphthalein	colourless	blue	9.4-10.5	9.3

methyl yellow, 0.4 g of bromothymol blue and 0.5g of thymol blue in 500ml of absolute alcohol, and add sufficient sodium hydroxide solution till the colour is yellow. The colour changes with this universal indicator are *p*H 2 red, *p*H 4 orange, *p*H6 yellow, *p*H8 green and pH10 blue.

Exercise 21.3. *To determine the pH of a given solution using pH indicators.*

Principle. Indicators are organic substances which change in colour with variations in the *p*H of the solution. The acid base indicators are dyes which behave like weak acids or weak bases. The indicators possess different colours in the ionised and unionised form, i.e.,

$$\underset{\text{unionised colour}}{HI_n} \rightleftharpoons H^+ + \underset{\text{ionised colour}}{I_n^-} \quad \ldots (21.6)$$

$$K_{I_n} = \frac{[H^+][I_n^-]}{[HI_n]} \quad \ldots (21.7)$$

or

$$[H^+] = K_{I_n} \times \frac{[HI_n]}{[I_n^-]} \quad \ldots (21.8)$$

Taking logarithm of both sides of equation (21.8)

$$\log[H^+] = \log K_{I_n} + \log \frac{[HI_n]}{[I_n^-]} \quad \ldots (21.9)$$

Multiplying both sides by −1

$$-\log[H^+] = -\log K_{I_n} - \log\frac{[HI_n]}{[I_n]}$$

$$pH = pK_{I_n} + \log\frac{[I_n^-]}{[HI_n]} \quad \ldots (21.10)$$

where,

$pK_{I_n} = -\log K_{I_n}$, is known as the apparent pK_{I_n} of the indicator

$$pH = pK_{I_n} + \log\frac{[\text{Ionised}]}{[\text{Unionised}]} \quad \ldots (21.11)$$

or

$$pH = pK_{I_n} + \log\frac{[\text{Base form}]}{[\text{Acid form}]} \quad \ldots (21.12)$$

The detection of colour change depends to some extent upon the colour perception of the individual indicator. Usually the average individual can detect 100 parts of one colour in the presence of 10 parts of the other colour, i.e.,

$$pH = pK_{In} + \log\frac{100}{10}$$

$$pH = pK_{In} + 1 \qquad \ldots (21.13)$$

The ideal indicator for use in determination of *p*H of a solution is one of which *p*K is nearly equal to the *p*H of the given solution.

A series of standard solution in the acid range are prepared by diluting a solution of strong acid. Similarly a series of standard solutions in the basic range are prepared by diluting a solution of a strong base. These solutions will serve as standards. The *p*H of the unknown solution can be determined by using appropriate indicator and companying the colour of the unknow with the colour of the standard solution. The approximate *p*H of the solution can be determined using universal indicators.

Procedure. Take 2ml of the given solution and determine its approximate *p*H using universial indicator. This will help in choosing suitable indicator. The indicator selected should have approximately the same pK_{In} value as the *p*H of the solution.

Take two sets of nine clean test tubes and label them as A1, A2, A3, A4, A5, A6, A7, A8, and A9 for acidic solutions and B1, B2, B3, B4, B5, B6, B7, B8, and B9, for basic solutions.

In each of the set test tubes labelled from A1 to A9 pour 10ml of a strong acid solution. In a similar manner pour 10ml of a strong base solution of same concentration in each of the test tubes labelled from B1 to B9. Pair the test tubes as under:

A1	B1
A2	B2
A3	B3
A4	B4
A5	B5
A6	B6
A7	B7
A8	B8
A9	B9

To the first pair add one drop of the indicator in A1 and nine drops of the indicator in B1. Similarly in the second pair add two drops of the indicator in the test tube labelled A2 and eight drops in B2. Add indicator in each pair of the test tubes in the same manner till the ninth pair contains 9 drops of the indicator in the test tube A9 and only one drop in B9. Thus each pair contains 10 drops of the indicator.

Now take 10ml of the given solution in the test tube labelled as G1 and add 10 drops of indicator. Pair it with a test tube G2 containing 10ml of water. Compare this colour with the mixed colour of the paired acid-alkali test tubes.

Method of calculation. Suppose the colour of the solution under test is matched with test tubes pair No. 8. This means that the indicator requires 8 parts of acid form and 2 parts of the base form. Relation (5) can be written as,

$$pH = pK_{I_n} + \log \frac{8}{2}$$

$$pH = pK_{I_n} + \log 4$$

The pK_{I_n} can be substituted from Table 21.1 and *p*H of the solution can thus be determined.

Result. The *p*H of the given solution is . . . .

Exercise 21.4. *To study the change in the pH of a weak acid (acetic acid) solution by common ion effect (sodium acetate).*

Principle. Suppose we have a solution of acetic acid this is ionised in solution producing acetate ions and hydrogen ions.

$$HAc \rightleftharpoons H^+ + Ac^-$$

If sodium acetate solution is added to the acid—this will ionise freely and the concentration of acetate ions will be increased. As a result of this more hydrogen ions will react with acetate ions and form undissociated molecules of acetic acid. Thus on adding sodium acetate to acetic acid, the ionisation of acetic acid will be suppressed and there will be a decrease in the hydrogen ion concentration. The *p*H of the solution which is a measure of hydrogen ion concentration, will thus be lowered. The approximate value of *p*H of a solution can be measured using indicator test paper or by multiple range indicator solution.

Procedure. Take two clean test tubes and label them 1 and 2, pour 10ml of 0.2M acetic acid in both the test tubes. In the tube 2 add 5ml of 17 sodium acetate solution. Now add 4-5 drops of universal indicator in both the test tube. Observe colour of the solution in both the test tubes which will be different. From the chart of the indicator used find out the approximate *p*H of the solution in tube 1 and tube 2. Record the observations.

Result. The *p*H of a weak acid solution is increased/decreased by common ion effect.

The large number of buffer mixtures have been recommended, including mixtures based on acetic, boric, citric, phosphoric, malonic and phthalic and oxalic acids and ammonium salts, and any *p*H from 1 to 10 can be obtained by making up suitable buffer solution. Table 21.2 gives the *p*H value and composition of the mixture.

TABLE 21.2

Buffer mixtures and their Composition

	Composition of mixtures	*pH*
1.	47.5ml N/5 HCl+25ml N/5 KCl mixture dilute to 100ml.	1
2.	5.3ml N/5 HCl+25ml N/5KCl mixture dilute to 100ml.	2
3.	20.55ml M/5 Na_2HPO_4+79.45ml M/10 citric acid.	3
4.	41 ml M/5 acetic acid+9.0ml M/5 sodium acetate.	4
5.	14.75ml M/5 acetic acid+9.0ml M/5 sodium acetate.	5
6.	11.00ml M/20 borax+29.0ml of a solution containing 12.40g. H_3BO_3 and 2.93 g NaCl in one litre.	8
7.	40.0ml M/20 borax+10.0ml of a solution containing 12.40g H_3BO_3	9
8.	Equal parts M/40 $NaHCO_3$ and M/40 Na_2CO_3	10

Universal indicators. If only the approximate *p*H of the solution is to be determined, certain mixed indicators which exhibit a variety of colours over a wide range of *p*H are used. These mixtures of different indicators are called universal indicators. They give only approximate *p*H value of the solution and are not suitable for quantitative measurements. Some of the mixed indicators (universal indicators) may be prepared as follows:

Indicators	*Amount*
1. Phenolphthalein	0.05g
2. Methyl red	0.1g
3. Methyl yellow	0.15g
4. Bromothymol blue	0.20g
5. Thymol blue	0.25g

Dissolve all the indicators given above in 250ml of absolute alcohol and add NaOH solution till the solution aquires a yellow colour. This will show the following colour changes at different *p*H's.

Colour of universal indicator	*pH*
Red	2
Orange	4
Yellow	6
Green	8
Blue	10

Another universal indicator, which can be prepared by dissolving:

Indicators	Amount
1. Phenolphthalein	0.35g
2. Methyl orange	0.05g
3. Methyl red	0.15g
4. Bromothymol blue	0.3g

in one litre of 66 per cent alcohol, exhibits the colour changes given below:

Colour change by the indicator	pH
Red	1-3
Orange red	4
Orange	5
Yellow	6
Yellow green	7
Greenish blue	8
Blue	9
Violet	10
Reddish violet	11

Some other mixed indicators may also be prepared by dissolving various indicators in certain ratios so as to give a suitable *p*H range.

22

Treatment of Experimental Data

22.1 INTRODUCTION

There are few, if any, absolute values in science, even though a majority of the experiments in science are quantitative in nature. Most values refer to a standard that has been arbitrarily fixed for the purpose of reference. Measurements make it possible to obtain more exact information about the properties of matter, such as size, shape, mass, temperature or composition. For example, the mass of an object can be more accurately determined by weighing it on a balance than by merely lifting it, similarly we measure time more accurately with the help of a clock than by observing with the naked eye the position of the sun in the sky.

The molecular and atomic weights are expressed with reference to the mass of an isotope of carbon which has been assigned the value 12.000. The number 12.000 was chosen arbitrarily and has no absolute significance. The ultimate object of performing a physical chemistry experiment is usually to obtain one or more numerical results. Between the recording of measured values and the reporting of numerical results there are processes of arithmetical calculation, some of which may involve averaging or smoothing the measured values but most of which involve the application of formulae derived from physics or physical chemistry.

Although great importance is given to measurement in an experiment. Yet all experimental measurements are subject to error. There is always some degree of uncertainty in every measurement, which may come from either (*a*) limitation of accuracy or (*b*) limitation of precision. Let us now understand the terms Error, Accuracy and Precision.

Error. Every physical quantity whose value is being determined is subjected to error in its determination. The difference between a measured value and a true value of an experimental quantity, is called Error. It should be understood to mean a departure from the true value and not a mistake on the part of the observer.

Accuracy. It involves comparison of the measured value with the true or accepted value.

Precision. It describes the reproducibility of results. It can be defined as the degree of agreement among several identical measurements. Measurements may be precise but may not necessarily be accurate. This situation arises when there is a constant source of error, which effects each measurement of a particular property in the same way.

The precision of a particular measurement depends on a number of factors, such as the nature of the apparatus used and the experience of the experimenter. Error in an experimental measurement can be classified into two types (*a*) Determinate errors, (*b*) Indeterminate errors.

Determinate errors. These are the errors that are introduced as a result of some inherent error in the method of measurement or in the calibration or manufacturing specification of the measuring device. Determinate errors affect every measurement of a set to the same extent. Some of the more common determinate errors are:

(*i*) *Instrumental errors*. This is due to the instrument or apparatus employed in measuring the quantity. No instrument is perfect, there is always a limit to its accuracy and it is important for the observer using the instrument to ascertain where this limit lies. All standard instrument makers provide the calibration data. Since the checking or calibration of an instrument usually requires the use of reliable standards for example, standard weights, thermometers, resistances, voltaic cells etc. These in turn have also been calibrated according to standard laboratory standards.

(*ii*) *Operational errors*. These errors are introduced as a result of inexperience or carelessness on the part of the experimenter and not to some flow in an apparatus or procedure.

(*iii*) *Personal errors*. These are due to an individual or personal limitation and are difficult to eliminate. For example error in judgement of a colour change during a titration by a person suffering from colorblindness is a personal error.

(*iv*) *Inherent errors*. An experimental procedure adopted in an experiment may suffer from certain inherent errors or the errors built in the method of calculations.

Determinate errors are also known as systematic errors. They are constant in magnitude because they do not depend on the magnitude of the property being measured. Some determinate errors are proportional to the amount of the sample used in the analysis. Certain errors will have the same sign. For example the incomplete expulsion of matter will always lead to positive error, whereas the solubility losses, incomplete reactions, and losses of materials during transfer, will always lead to negative errors.

(*v*) *Indeterminate errors.* These errors are also known as random errors because they follow the law of chance.or probability. They are present inspite of the best efforts made by the experimenter. The indeterminate errors are governed by the following rules:

(*a*) small errors occur more frequently than large ones.

(*b*) positive and negative error occur with equal frequency. The most probable value is given by the arithmetic mean of the measured values.

In an experimental determination of a quantity let X_1, X_2, X_3 .... X_n be the N measured values in a set of observations. The arithmetic mean is defined as:

$$X=\frac{X_1+X_2+X_3\ldots\ldots+X_n}{N} \qquad \ldots(22.1)$$

The difference between the observed value X_1 and the true value T is equal to the error.

$$\text{Error }=X_1-T \qquad \ldots(22.2)$$

$$\text{Relative Error}=\frac{\text{Error}}{T} \qquad \ldots(22.3)$$

The ratio is often multiplied by 100, 1000, or 1,000,000 and expressed as percentage (%), parts per thousand (p.p.t) or parts per million (p.p.m.) respectively.

The deviation, di, of an individual value is defined as the difference between the mean a set of measurements and the individual measurement,

$$d_i\phi=X-X_i$$

The average diviation d, is the sum of the deviations for the individual values divided by the total number of values:

Standard deviation (σ) is defined as the square, not of the sum of the squares of the individual deviations divided by the square root of N−1.

The term N—1 is called the degrees of freedom and is equal to one less than number of measurements.

Normal distribution curve. If we make a large number of measurements on a quantity having its true value equal to T, all individual measurements will not be identical to T and will be rather scattered about T due to random error. If we plot the experimental results of an experiment i.e. an absolute error of such measurement against the frequency with which a given absolute error and sign occurs a normal error curve or normal frequency curve is thus obtained. The breadth of the curve indicates the precision of the measurement. A curve that is sharply peaked and drops off rapidly for large errors corresponds to a more precise method.

Significant figures. An experimental quantity is usually expressed by a number. A significant figure denotes the quantity in the place in which, it stands. The significant figures in a number are the digits in that number which are needed to express the precision of the measurement from which the number was obtained.

The significant figures in a number are the digits whose values are known with reasonable certainty *plus* one digit whose value is uncertain. For example the number 0.357, 3.57, and 357 all contain three significant figures. But if these values have been obtained in a computation involving muliplication or division of measured quantities, the values 3 and 5 are, reasonably certain, where as the 7 is an uncertain value. The following rules should be applied in the computation of analytical data.

(*a*) When the last digit dropped is 5 or greater than 5 increase by one the last digit. If the last digit in the number 348.87 is 7. The number after dropping the last digit will be 348.9.

(*b*) If the last digit dropped is less than 5 the last digit retained remains unchanged. For example if the last digit in 2.483 is rejected the rounded off number would be 2.48.

(*c*) When the last rejected digit is 5 increase by one the last digit retained if it is an odd number. Thus the value 275.5 would be rounded to 276. But if the last digit is an even number, it remains unchanged i.e. 274.5 would be rounded to 274.

There are some mathematically defined quantities such as integers, π and e, that may be known to as many decimal places as desired, and that for all practical purposes passes no uncertainty. In other words these are known with much greater certainity than the experimental quantities with which these are associated in computation.

Objective Type Questions

VOLUMETRIC ANALYSIS

1. What is meant by a normal solution and a molar solution?
2. Define gram equivalent weight of a substance.
3. Express the concentration of 3N H_2SO_4 in (*a*) grams per liter, (*b*) moles per liter, (*c*) gram equivalents per liter.
   Ans. (*a*) 147.1 g/liter, (*b*) 1.5 moles/liter, (*c*) 3 gram equiv/liter.
4. If 200 ml of sulphuric acid solution contain 2.450 g of H_2SO_4, calculate the molarity and normality of the solution.
   Ans. 0.125 M, 0.2500 N.
5. What condition must be fulfilled in a volumetric titration?
6. Is the gram-equivalent of a substance a constant value?
7. Calculate the gram equivalent of the following substances:
   (*a*) H_2SO_4 (*b*) $Na_2CO_3.10H_2O$ (*c*) $Na_2B_4O_7.10H_2O$
   Ans. (*a*) 49.04g (*b*) 143.07 (*c*) 190.69.
8. What solutions are called standard solutions?
9. In what ratio by volume do solutions of the same normality react?
10. How many milliliters of 0.1N HCl solutions are needed to neutralise (*i*) 10ml of 0.1N Ca $(OH)_2$ (*ii*) 10ml of 0.1N NaOH, (*iii*) 10.00ml of 1.0N NaOH, (*iv*) 10.00ml of 0.05N NH_4OH solution.
11. What quantity of chemically pure $Na_2B_4O_7$. $10H_2O$ is required to prepare 200ml of 0.1 N solution?
    Ans. 3.8138g.
12. What is an indicator?
13. Distilled water is always used in the preparation of standard solution. Why?
14. How much water must be added to 1 liter of 0.250 N HCl solution to obtain a 0.2N solution?
    Ans. 250ml.
15. What volume of H_2SO_4 of density 1.202g/ml must be diluted with water to obtain 3 liters of 0.1N acid?
    Ans. 43.7ml.
16. Why is chemically pure borax used as a primary standard for determining the normality of standard acid solution ?
17. What standard solution and indicator are used in the permanganate method?
18. How are reducing and oxidising agents analysed by titration with potassium permanganate?
19. Against what chemically pure substance is the normality of $KMnO_4$ solution usually determined?
20. Why is HCl or HNO_3 not used in place of dil H_2SO_4 in the titrations involving $KMnO_4$?
21. How is the gram-equivalent of an oxidising or reducing agent determined?

22. The colour of $KMnO_4$ disappears slowly in the beginning and very rapidly afterwards when titrated against oxalic acid (60°C) containing dil H_2SO_4. Explain.
23. A brown turbidity is sometimes noticed in the above titration. Why?
24. A liter solution contains 0.3161 g $KMnO_4$. Determine the normality of this solution, and its titre in terms of iron.
    Ans. 0.010N; 0.0005585g/ml.
25. What are external indicators? Name the External indicator employed in the titration of Fe^{2+} with potassium dichromate.
26. In the estimation of iron with $K_2Cr_2O_7$, what is the purpose of adding mixed acids before titration?
27. A fresh solution of potassium ferricyanide indicator must be employed for dicharomate titration. Why?
28. "Phosphoric acid is added when diphenylamine is used as an indicator." Explain the statement.
29. What standard solutions and indicator are used in Iodometry?
30. Why is iodine regarded as secondary standard substance?
31. What is the gram-equivalent of sodium thiosulphate in its reaction with iodine?
32. Why is an excess of potassium iodide used in iodometric analysis?
33. How are thiosulphate and iodine solutions standardised?
34. What is the difference between Iodometry and Iodimetry?
35. Why a fresh solution of starch is used in the iodometric titration?
36. Why should the starch solution added near the end point?
37. Why must acidic solutions be diluted with a large amount of water prior to titrating them with thiosulphate solution?
38. Explain why sodium bicarbonate is added in the titration of sodium arsenite with standard iodine solution?
39. Why is it essential to use a neutral solution of copper sulphate in iodometric titrations?
40. Why is ammonium thiocyanate added in the iodometric estimation of copper sulphate?
41. Name the standard solutions and indicators used in argentometric titrations.
42. Why is nitric acid added in Volhard's method for the estimation of silver nitrate?
43. What substances are determined by argentometric analysis?
44. How is silver nitrate solution standardised?
45. In what cases is argentometric method unsuitable for determining the content of chlorides?
46. Why should the reaction mixture be kept vigorously shaken in Volhard's method for the estimation of $AgNO_3$?
47. Why should K_2CrO_4 be used in neutral solution of halides?
48. Why Mohr's method cannot be used for determination of iodide?
49. State the conditions which a given precipitation reaction, must satisfy before it can be used in volumetric analysis.
50. Determine the normality of a sodium chloride solution that contains 1.4615g of NaCl in 200 ml of solution.
    Ans. 0.125 N.
51. Calculate the normality of a $AgNO_3$ solution whose titre in terms of

NaCl is equal to 0.002923g/ml.

Ans. 0.0500 N.

52. How will you prepare a centinormal solution from given decinormal solution?
53. Is there any difference between end point and equivalence point?
54. What is stoichiometric point?
55. Why penolphthalein does not serve as a suitable indicator for the titration of HCl versus Na_2CO_3?
56. Why $KMnO_4$ acts as a self-indicator?
57. Only initial heating is required in the estimation of oxalate ions by $KMnO_4$. Explain.
58. A student is always advised to remove the funnel from the burette, before starting titration, give reason.
59. If some water is added to the solution taken in titration flask by pipette, will it affect the titration?
60. Why is dilute H_2SO_4 is added in the $KMnO_4$ versus ferrous ammonium sulphate titration? Can you use conc. H_2SO_4 in place of dil H_2SO_4?
61. In the iodometric estimation of $Cr_2O_7^{2-}$, the end point is light green. Give reason.
62. Why $K_3Fe(CN)_6$ is not used as an internal indicator in the estimation of Fe^{2+} ion by $Cr_2O_7^{2-}$?
63. Why is iodine solution prepared in KI?
64. Explain the function of the following in the iodometric estimation of
    (*a*) Ammonium hydroxide.
    (*b*) Acetic acid.
    (*c*) Ammonium thiocyanate.
65. Why is ammonium thiocyanate added just near the end point in the titration of $CuSO_4$ versus sodium thiosulphate?
66. What is the oxidation state of antimony in tartar emetic?
67. Why is it essential to remove hydrogen iodide, from the sphere of action, formed during the iodimetric estimation of arsenious oxide?
68. Can you prepare a standard solution of sodium thiosulphate?
69. Why is silver nitrate solution always prepared only in distilled water?
70. In the argentometric estimation of Cl^-ions by Mohr's method AgCl precipitates earlier than Ag_2CrO_4. Explain.

GRAVIMETRIC ANALYSIS

1. The precipitation of barium should be carried out in the presence of 0.05 N-HCl solution. Why?
2. Why should large excess of HCl be avoided?
3. How can you avoid coprecipitation of $BaCl_2$ with $BaSO_4$?
4. Is it necessary to remove Cl^- and SO_4^{2-} ions from the precipitate before drying?
5. Why the ignition of the $BaSO_4$ ppt should be carried out below 600°C?
6. Why the residue is treated with 2 drops of conc. HCl and 2 drops of conc. H_2SO_4?
7. What is a conversion factor? Calculate the conversion factor for finding the amount of Ba^{2+} and SO_4^{2-} from the weight of $BaSO_4$?
8. Explain why:

(*a*) Solutions in gravimetric estimations are generally heated before the precipitation as well as after the precipitation.

(*b*) A given solution in gravimetric estimation is diluted before precipitation.

(*c*) A great excess of precipitating reagent is avoided.

(*d*) Precipitant is added drop by drop.

9. How will you prepare paper pulp in the laboratory ?

   Explain why

   (*a*) The use of filter paper is recommended during the precipitation of iron and aluminium.

   (*b*) Excess of NH_4OH should be avoided in the precipitation of Al $(OH)_3$.

   (*c*) Ignition of Al $(OH)_3$ ppt should be done at high temperature.

   (*d*) Al_2O_3 residue should be weighted quickly.

10. Explain why ferrous salt solution is heated with conc. HNO_3 before precipitation?
11. Why in NH_4NO_3 solution used in the estimation of iron?
12. Why final ignition of precipitate in iron determination be done at 1000°C?
13. Excess of NH_4OH is added during the precipitation of iron. Explain.

    The washing of $Fe(OH)_3$ precipitate should be done immediately after precipitation. Why?
14. Can we use KOH solution in place of NaOH solution as precipitant for copper?
15. Can NH_4OH be used in place of NaOH solution as a precipitating agent, during the precipitation of copper as Cu $(OH)_2$?
16. How does acidity/alkalinity influence the completion of precipitation of Ni^{2+} with dimethylglyoxime?
17. Why drying of nickel dimethylglyoxime precipitate should be done at 100-120°C and not at higher temperature?
18. What is the function of sulphurous acid in the estimation of copper (Cu^+) as CuCNS?
19. Why the oxidising agent should be absent in the gravimetric estimation of copper as CuCNS?
20. Why the precipitate is washed with ammonium thiocyanate, and sulphurous acid?

ORGANIC CHEMISTRY

1. What is the effect of a thick-walled capillary tube on the observed melting point of a substance?
2. How does rapid heating affect the observed melting point?
3. It is always advised to run a mixed melting point on samples of two different compositions before concluding that the two compounds used were identical ? Explain.
4. Predict the effect of the presence of a pin-hole in the bottom of the capillary-tube, on the observed melting point.
5. What is the effect of sand on the melting point of ice?

6. How is the freezing point of benzene affected by NaCl?
7. Why cold water is circulated through a condenser from the bottom upwards rather than from the top downward?
8 Why does not all of the liquid in the distilling flask vaporise at once when the boiling point is reached?
9. What is the disadvantage of filling a distillation flask much more than half-full?
10. Why should, a distilling flask having capacity four or five times the volume of the liquid being distilled, be not used?
11. An organic liquid begins to decompose at 100°C. its vapour pressure at that temperature is 45 mm. How would you distil the liquid?
12. How do you explain that acetone and ethyl alcohol lower the melting point of ice as well as the boiling point of water, whereas salt and sugar raise the boiling point and lower the melting point?
13. What effect do (*a*) ether and (*b*) benzoic acid have on the boiling point and melting point of benzene?
14. If the thermometer bulb is not kept moist with condensate during a distillation, will the boiling point reading tend to be high or low? Explain.
15. What effect does each of the following impurities have on the boiling point of water and the melting points of ice?
    (*a*) Sand, (*b*) Ethyl alcohol, (*c*) Sugar and (*d*) Chloroform.
16. A student suspected that an unknown was undergoing a chemical change at its melting point. Suggest a simple method for testing his hypothesis.
17. During cooling process for crystallization, is it advisable to cool the solution slowly or rapidly? Explain.
18. What advantages does water have as a crystallization solvent?
19. It is always advised to break the suction before turning off the water pump in collecting a solid by suction filtration. Explain.
20. Why is it important to minimize evaporation during the filtration of the hot solution?
21. Ethyl iodide is insoluble in water but in ethyl alcohol is soluble. Explain.
22. Why activated charcoal is used as a good absorbing agent?
23. Suggest a good solvent for each of the following
    (*i*) Benzoic acid (*ii*) Succinic acid (*iii*) Naphthalene
    (*iv*) Sodium butyrate and (*v*) acetanilide.
24. Explain the order in boiling points of the following solvents: acetic acid ethyl alcohol and methyl alcohol.
25. Hydrocarbons and their halogen derivatives are virtually insoluble in water. Explain.
26. Why the medium sized crystals are preferred?
27. Why must hydrogen cyanide or hydrogen sulphide be expelled before a test is made for the halide ion?
28. A student was given urea for the detection of elements, but he obtained a positive test for halogen. What error in his procedure would account for this result?
29. Sometimes, one gets light green colour in the solution while detecting for nitrogen by Lassaigne's test, offer a suitable explanation for this.
30. In the detection of nitrogen, why the solution is boiled after adding $FeSO_4$.

31. In the carbon tetrachloride test for bromine and iodine, why does the lower layer gives the characteristic colour?
32. What is the function of dilute sulphuric acid in Lassigne's test for nitrogen?
33. What elements are found in organic compounds isolated from natural sources?

PHYSICAL CHEMISTRY

Surface Tension Viscosity

1. What is the origin of surface tension?
2. What are the units of surface tension?
3. Comment on the difficulty of estimation fractions of a drop, and suggest an improvement in the technique which would reduce or eliminate this source of error.
4. Why must the drop rate not be too great?
5. Why in general it is inadvisable to use water to calibrate a stalagnometer for use with organic liquids?
6. Discuss the experimental errors and theoretical uncertainties and quote the surface tensions up to the appropriate number of significant figures.
7. Discuss the use of stalagmometer in determining the interfacial surface tensions.
8. Why is it necessary to ensure that the viscometer is mounted vertically?
9. Discuss the errors which would result from too fast a flow in the capillary of the viscometer.
10. What are CGS and SI units of viscosity.
11. What is the effect of temperature on the surface tension of a liquid.
12. At what temperature surface tension of a liquid will be zero.
13. What is inter-facial tension ?
14. What is the effect of temperature on the viscosity of a liquid ?
15. What is the effect of temperature on the viscosity of a gas ?
16. Explain the difference in the origin of viscosity of a liquid from that of viscosity of a gas.
17. What are the uses of viscosity and surface tension in pharmacy ?
18. Does the viscosity of the blood increases or decreases when a person has a high fever ?

Partition Coefficient

19. In the titration of iodine with sodium thiosulphate, why should starch solution should not be added too soon? Why is it unnecessary to standardise the sodium thiosulphate solution?
20. What errors can be introduced by blowing too much through the pipette when it is inserted into the carbon tetrachloride?
21. Under what circumstances the value of a distribution coefficient be expected to depend on concentration?

Transition Temperature Colloids

22. Why is the rate of cooling reduced to virtually zero at the transition point and why should a large degree of supercooling be avoided?

23. Discuss the relative magnitudes of the molar depressions of the additives, having in mind that the concentration of additive is high.
24. What is the physical cause of partial immisicibility as observed in the phenol-water system CST experiment. Account for the effect of impurities on critical solution temperature.
25. Explain why the concentration of gold sol is unimportant and yet it is necessary to use 10 ml in each test?
26. Why is the gold sol coloured? Estimate to an order of magnitude the size of the gold particles.
27. Suggest a reason why suitable substances are able to protect the gold sol from the coagulating action of the sodium chloride.

Chemical Kinetics

28. Why should the ester solution be dilute? **How is k related to the true** constant?
29. How might you determine the order **with respect to water and the variation** of k with the hydrogen ion concentration? Do you think that the 'quenching' of the reaction by the suggested dilution of the sample is adequate?

Molecular weight determination

30. Why should the inner tube not come into contact with water in the outer jacket?
31. What is the object of equalising the water levels inside and outside the graduated tube before reading the volume of gas therein?
32. The temperature of the vapour is 100°C, while that of the air displaced is only 20°C : Why does this not matter?
33. What is a tie-line?

Conductometric Titration

34. Explain, why it is necessary to know the cell constant of the conductance cell?
35. Why is it preferable for the titrating solution to be of a much higher concentration than that of the solution to be titrated?
36. Why must large amounts of non-precipitating electrolytes be excluded form conductometric titrations?
37. Show that the correction for the volume change of the solution during titration is given by $R' = R\,(V+v)/V$, here R' is the corrected resistance V is the original volume of the solution and v is the volume of the titrating solution.

Phase Equilibria

38. Why is the rate of cooling reduced when solid begins to separate from the melt?
39. Why must the large degrees of supercooling avoided ?
40. Why is there a break in the cooling curve at the freezing point and why is the break less marked for the solutions than for the pure substances?
41. What is an ideal solution? What factors determine whether or not a solution will behave ideally?
42 What is the ente point?

APPENDIX A-1

International Atomic Weights
Based on $C^{12}=12.000$

Element	*Symbol*	*Atomic Number*	*Atomic Weight*
Actinium	Ac	89	(227)*
Aluminium	Al	13	26.9815
Americium	Am	95	(243)*
Antimony	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74 9216
Astatine	At	85	(210)*
Barium	Ba	56	137.74
Berkelium	Bk	97	(247)*
Beryllium	Be	4	9.01218
Bismuth	Bi	83	208 9806
Boron	B	5	10.81
Bromine	Br	35	79.904
Cadmium	Cd	48	112.40
Calcium	Ca	20	40.08
Californium	Cf	98	(251)*
Carbon	C	6	12.011
Cerium	Ce	58	140.12
Cesium	Cs	55	132.9055
Chlorine	Cl	17	35 453
Chromium	Cr	24	51.996
Cobalt	Co	27	58.9332
Copper	Cu	29	63.546
Curium	Cm	96	(247)*
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(254)*
Erbium	Er	68	167.26
Europium	Eu	63	151 96
Fermium	Fm	100	(253)*
Fluorine	F	9	18.9984
Francium	Fr	87	(223)*
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69 72
Germanium	Ge	32	72.59
Gold	Au	79	196.9665
Hafnium	Hf	72	178.49
Helium	He	2	4 0026
Holmium	Ho	67	164.930

*Mass of most stable or best known isotope.

**Mass of most commonly available, long-lived isotope.

Element	*Symbol*	*Atomic Number*	*Atomic Weight*
Hydrogen	H	1	1.0080
Indium	In	49	114.82
Iodine	I	53	126.9045
Iridium	Ir	77	192.22
Iron	Fe	26	55.847
Krypton	Kr	36	83.80
Lanthanum	La	57	138.9055
Lawrencium	Lr	103	(257)*
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.305
Manganese	Mn	25	54.9380
Mendelevium	Md	101	(256)*
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.179
Neptunium	Np	93	237.0482**
Nickel	Ni	28	58.71
Niobium	Nb	41	92.9064
Nitrogen	N	7	14.0067
Nobelium	No	102	(254)*
Osmium	Os	76	190.2
Oxygen	O	8	15.9994
Palladium	Pd	46	106.4
Phosphorus	P	15	30.9738
Platinum	Pt	78	195.09
Plutonium	Pu	94	(242)*
Polonium	Po	84	(210)*
Potassium	K	19	39.102
Praseodymium	Pr	59	140.9077
Promethium	Pm	61	(147)*
Protactinium	Pa	91	231.0359*
Radium	Ra	88	226.0254**
Radon	Rn	86	(222)*
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.9055
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Samarium	Sm	62	150.4
Scandium	Sc	21	44.9559
Selenium	Se	34	78.96

*Mass of most stable or best known isotope.

**Mass of most commonly available, long-lived isotope.

Element	*Symbol*	*Atomic Number*	*Atomic Weight*
Silicon	Si	14	28.086
Silver	Ag	47	107.868
Sodium	Na	11	22.9898
Strontium	Sr	38	87.62
Sulfur	S	16	32.06
Tantalum	Ta	73	180.9479
Technetium	Tc	43	98.9062**
Tellurium	Te	52	127.60
Terbium	Tb	65	158.9254
Thallium	Tl	81	204.37
Thorium	Th	90	232.0381**
Thulium	Tm	69	168.9342
Tin	Sn	50	118.69
Titanium	Ti	22	47.90
Tungsten	W	74	183.85
Uranium	U	92	238.029
Vanadium	V	23	50.9414
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.9059
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22
Kurchatovium	Ku	104	(260)*
Hahnium	Ha	105	(260)*

APPENDIX A-2

Some Formula Weights

AgBr	187.78	KCl	74.56
AgCl	143.32	$KClO_4$	138.55
AgI	234.77	$KHC_8O_4O_4$ (KHP)	204.23
$AgNO_3$	169.88	KI	166.01
As_2O_3	197.84	KIO_3	214.00
As_2O_5	229.84	$KMnO_4$	158.04
$BaCl_2$	208.25	KOH	56.11
$BaCl_2.2H_2O$	244.27	KSCN	97.18
$BaCrO_4$	253.33	K_2CrO_4	194.20
$Ba(OH)_2$	171.36	$K_2Cr_2O_7$	294.19
$BaSO_4$	233.40	$MgCO_3$	84.32
CO_2	44.01	MnO_2	86.94
$CaCO_3$	100.09	NH_3	17.03
CaC_2O_4	128.10	NH_4Cl	53.49
CaO	56.08	NH_4OH	35.05
$Ca(OH)_2$	74.10	$(NH_4)_2SO_4$	132.14

CuO	79.54	NaBr	102.90
$CuSO_4.5H_2O$	249.68	NaCl	58.44
FeO	71.85	NaF	41.99
Fe_2O_3	159.62	$NaHCO_3$	84.01
Fe_3O_4	231.54	NaOH	40.00
HCO_2CH_3 (HAc)	60.05	Na_2CO_3	105.90
HCl	36.46	$Na_2H_2Y.2H_2O$ (EDTA)	372.24
HIO_4	191.91	$Ni(C_4H_7O_2N_2)_2$	288.94
HNO_3	63.02	$Ni(DMG_2)$	
$H_2C_2O_4$ (oxalic acid)	90.04	$PbCl_2$	278.10
$H_2C_2O_4.2H_2O$	126.07	$PbCrO_4$	323.19
H_2S	34.08	$PbSO_4$	303.25
H_2SO_4	98.08	Pb_3O_4	685.57
H_3PO_4	98.00	SO_2	64.06
KBr	119.01	ZnO	81.37
$KBrO_3$	167.01		—

APPENDIX A-3

Preparation of some common Desk Reagents

1. Hydrochloric acid, HCl, 6N (dil) Dilute the commercial concentrated HCl (sp. gravity 1.19, 37%) with an equal volume of water.
2. Nitric acid, HNO_3, 6N (dil). This may be prepared by diluting 380ml of concentrated nitric acid (69%. HNO_3 sp. gravity 1.42) with water to 1 liter.
3. Sulphuric acid, H_2SO_4, 18N (dil). Pour 465ml of the commercial concentrated sulphuric acid (95% H_2SO_4. sp. gravity 1.84) slowly into water and dilute to 1 liter.
4. Acetic acid, $C_2H_4O_2$, 6N. Dilute 350ml of glacial acetic with water to 1 liter.
5. Ammonia, NH_3, 6N. Dilute 400ml of the concentrated ammonia of commerce (28% NH_3, sp. gravity 0.90) with water to 1 liter.
6. Sodium Hydroxide, NaOH, 6N. Dissolve 240g of solid NaOH in water to make 1 liter of solution.
7. Silver Nitrate, $AgNO_3$, 0.5M. Dissolve 85g of solid $AgNO_3$ in water and dilute to 1 liter capacity. The solution should be prepared in distilled water.
8. Ammonium chloride, NH_4Cl, 3M. Dissolve 160g of NH_4Cl in water and make up to 1 liter.
9. Ammonium carbonate, $(NH_4)_2CO_3$, 1.5M. Dissolve 171g of the hydrate $(NH_4)_2CO_3$. H_2O in water and dilute to 1 liter.
10. Potassium dichromate, $K_2Cr_2O_7$, 0.5M. Dissolve 147g of $K_2Cr_2O_7$ in water and dilute to 1 liter.

APPENDIX A-4

Method of Preparations of some Special Reagents

1. 2,4 Dinitrophenylhydrazine
   Dissolve 2g of 2,4—dinitrophenylhydrazine in 15ml of conc. H_2SO_4. Add the solution to 150ml of 95% ethanol. Dilute the mixture to 500ml with distilled water. Mix thoroughly and filter, if necessary.
2. Ceric ammonium nitrate
   Dissolve 20g ceric ammonium nitrate in 500ml of warm 2N nitric acid.
3. Iodine Solution
   Dissolve 10g iodine and 25g potassium iodide in 100ml distilled water.
4. Chlorine water
   Pass chlorine gas in cold water till a saturated solution is obtained.
5. Molisch reagent
   Dissolve 10g α-naphthol in 100ml of 95% ethanol.
6. Phenolpthalein
   Dissolve 1g phenolphthalein in 100ml of 95% ethanol.
7. Aluminon
   Dissolve 0 25g of alumion in 250ml of distilled water.
8. Dimethyl glyoxime
   Dissolve 1g of dimethyl glyoxime in 100ml of 95% ethanol.
9. Diphenylamine
   Dissolve 0.5g of diphenylamine in 100ml pure conc. H_2SO_4 and dilute with 25ml of distilled water.
10. Lanthanum Nitrate
    Dissolve 5.0g of lanthanum nitrate in 100ml of distilled water.
11. Magneson II
    Dissolve 1g magneson—II in 1 litre of the solution containing 20g of sodium hydroxide.
12. α—naphthylamine.
    Dissolve 0.3g of α-naphthylamine in 70ml hot distilled water. Add 30ml of glacial acetic acid.
13. Nessler's reagent
    Dissolve 50g of KI in 50ml of water, to the resulting solution add gradually a saturated solution of $HgCl_2$ (6g per 100ml of water) until a stable precipitate of HgI_2 appears, then add 200ml of 6N NaOH and dilute to 500ml with water, keep in a dark place.
14. Schiff's Reagent
    Dissolve 1g of rosaniline in 50ml of water with gentle warming. Cool, saturate with SO_2, add about 1g. of animal charcoal, shake and filter; make upto one liter with water. If the pink colour reappears on standing, add a few drops of SO_2—water carefully with stirring until the colour just dissappears.
15. Methyl Orange
    Dissolve 1g of methyl-orange in 1.5 litres of boiling water.
16. Hydrogen Peroxide
    "10 volumes" solution (as purchased).
17. Fehling—Solution

Solution A. Dissolve 69.28g of $CuSO_4$. $5H_2O$ in water and make up to one liter.

Soulotion B. Dissolve 346g of sodium potassium tartrate (CH_4O_6NaK. $4H_2O$ Rochelle salt) and 120g of NaOH in water and make the mixed tartrate and hydroxide solution upto one liter.

To prepare Fehling's solution, mix equal volumes of solution A&B.Fehling's solution should be prepared only in sufficient quantity for immediate needs, as it slowly deteriorates on standing, while solutions A&B keep almost indefinitely.

18. Tollens' Reagent.

Dissolve 30g of silver nitrate in 500ml of water and add a solution of ammonium hydroxide until the precipitate of silver oxide which first forms is redissolved. Dilute the solution to one litre. The solution may be used in this form. For higher sensitivity, a portion of the solution should be mixed immediately before use with an equal volume of a 5% solution of sodium hydroxide, when heated or allowed to stand for a long period, this mixture deposits a black precipitate which is explosive.

19. Lucas' Reagent

Dissolve 136g of anhydrous zinc chloride in 105g of concentrated hydrochloric acid, with cooling.

20. Ferric Chloride, 0.2 M

Dissolve 50g of $FeCl_3$. $6H_2O$ in 10ml of 12N-HCl and 990ml of water.

21. Lead Acetate, 0 5M

Dissolve 190g of $Pb(C_2H_3O_2)_2$. $3H_2O$ in water and dilute to one litre.

22. Potassium Chromate, 0.3M

Dissolve 55g of K_2CrO_4 in water and dilute to one liter.

23. Potassium Ferrocyanide, 0.05M

Dissolve 21g of $K_4[Fe(CN)_6]$. $3H_2O$ in water and dilute to one liter.

24. Potassium Ferricyanide, 0.06M

Dissolve 22g of $K_3Fe(CN)_6$ in water and dilute to one litre.

25. Sodium cobaltinitrite, 0.1M

Dissolve 230g of $NaNO_2$ and 35g of $Co(NO_3)$. $6H_2O$ in 60ml of glacial acetic acid and dilute with water to make one litre.

Appendix A-5

Density of wate? at various temperatures

Temperature *t(°C)*	*Density* *(kg/l)*	*Temperature* *t(°C)*	*Density* *(kg/l)*
0	999.846	21	997.995
4	999.972	22	997.772
5	999.964	23	997.540
6	999.941	24	997.298
7	999.903	25	997.045
8	999.850	26	996.783
9	999.784	27	996.512

Contd. on page 302

APPENDIX A-6

Viscosities of Liquids (milkpoise)

Substance	*0°C*	*10°C*	*15°C*	*20°C*	*25°C*	*30°C*	*40°C*	*50°C*
Aniline	122.0	64.5	53.3	42.7	36.4	31.1	23.6	18.6
Ethyl alcohol	17.72	14.66	13.0	12.00	10.78	10.03	8.34	7.02
Methyl alcohol	8.08	6.90	6.23	5.92	5.44	5,15	4.49	3.95
Benzene	9.00	7.57	6.96	6.47	5.96	5.61	4.92	4.36
Carbon tetra-chloride	13.51	11.38	10.40	9.75	9.03	8.48	7.46	6.62
Chloroform	6.99	6.25	5 96	5.63	—	5.10	4.64	4.24
Toluene	7.72	6.71	6.23	5.90	—	5.25	4.71	4.26
Water	17.865	13.04	11.37	19.2	18.91	7.98	6.54	5.477

APPENDIX A-7

Surface Tension of Liquids

Substance	*0°C*	*10°C*	*15°C*	*20°C*	*25°C*	*30°C*	*40°C*	*50°C*
Water	1.564	7.422	7.349	7.275	7.197	7.118	6.956	6.791
Ethyl alcohol	2.405	2.312	2.276	2.227	2.185	2 143	2.060	1.980
Ethyl acetate	2.65	—	2.436	2.39	—	2.255	—	2.02
Carbon tetra-chloride	2.94	2.800	2.736	2.677	2.614	2.533	2.441	2.314
Ethyl ether	—	—	1.762	1.701	1.650	1.595	—	1.347
Benzene	3.158	3.022	2.955	2.888	—	2.756	2.626	2.498

Contd. from page 300

10	999.703	28	996.232
11	999.609	29	995.943
12	999.502	30	995.646
13	999.382	31	995.300
14	999.249	33	995.040
15	999.104	33	994.705
16	998.948	34	994.400
17	998.780	35	994.080
18	998.600		
19	998.409		
20	998.207		

APPENDIX A—8

General Properties of some organic liquids

Compound	*Density* kgm^{-3} (298K)	*Refractive index* (293K)	*Viscosity* (298K)	*Surface tension* (293K)
Acetic acid	1044.0	1.3716	11.55	27.8
Acetone	785.0	1.3588	3.16	23.7
Aniline	1022.0 (293K)	1.5863	3.71	42.9
Benzene	874.0	1.5011	6.01	28.89
Carbon tetrachloride	1584.0	1.4601	8.7	26.95
Chlorobenzene	1106.0	1.5241	7.97	33.56
Cyclohexane	774.0	1.4266	9.8	25.5
Ethylacetate	900.0	1.3723	4.41	23.9
Ethanol	785.0	1.3611	10.0	22.75
Hexane	655.0	1.37506	2.94	18.43
Methanol	787.0	1.3288	5.47	22.61
Toluene	862.0	1.4961	5.50	28.50

APPENDIX A—9

Heat of solution values of some salts

Substance	*Moles of* H_2O *per mole of salt*	ΔH *solution kcal/mole*	*Substance*	*Moles of* H_2O *per moles of salt*	ΔH *solution kcal/mole*
NaCl	200	+ 1.28	$MgSO_4 7H_2O$	400	+23.80
KNO_3	200	+ 8.52	Na_2SO_4	400	− 0.55
NH_4Cl	200	+ 3.88	Na_2SO_4 $10H_2O$	400	+18.90
$BaCl_2 2H_2O$	400	+ 4.93	KCl	200	+ 4.20
$CuSO_4$ (anhydrous)	400	−15.80	H_2SO_4(l)	200	−17.91
$CuSO_4 5H_2O$	400	+ 2.75	KOH(s)	5	−11.53
NH_4NO_3(s)	5	+ 4.24		—	—

APPENDIX A-10

Buffer Mixtures for pH Determinations
Phosphate Mixtures for the pH Range 2.2-8.0

pH	*0.2 M Na_2HPO_4, ml*	*0.1 M Citric acid, ml*	*pH*	*0.2 M Na_2HPO_4 ml*	*0.1 M Citric acid, ml*
2.2	0.40	19.60	5.2	10.72	9.28
2.4	1.24	18.76	5.4	11.15	8.85
2.6	2.18	17.82	5.6	11.60	8.40
2.8	3.17	16.83	5.8	12.09	7.91
3.0	4.11	15.89	6.0	12.63	7.37
3.2	4.94	15.06	6.2	13.22	6.78
3.4	5.70	14.30	6.4	13.85	6.15
3.6	6.44	13.56	6.6	14.55	5.45
3.8	7.10	12.90	6.8	15.45	4.55
4.0	7.71	12.29	7.0	16.47	3.53
4.2	8.28	11.72	7.2	17.39	2.61
4.4	8.82	11.18	7.4	18.17	1.83
4.6	9.35	10.65	7.6	18.73	1.27
4.8	9.86	10.14	7.8	19.15	0.85
5.0	10.30	9.70	8.0	19.45	0.55

APPENDIX A—11

Universal Mixtures for the pH Range 1.81-11.93 (at 18° C) V ml of 0.2 N NaOH solution is added to 100 ml of a mixture of equal volumes of 0.04 M H_3PO_4, 0.04N CH_3COOH, and 0.04 M H_3BO_3

V	*pH*	*V*	*pH*	*V*	*pH*	*V*	*pH*
0	1.81	27.5	4.35	52.5	7.00	77.5	9.91
2.5	1.89	30.0	4.56	55.0	7.24	80.0	10.38
5.0	1.98	32.5	4.78	57.5	7.54	82.5	10.88
7.5	2.09	35.0	5.02	60.0	7.96	85.0	11.20
10.0	2.21	37.5	5.33	62.5	8.36	87.5	11.40
12.5	2.36	40.0	5.72	65.0	8.69	90.0	11.58
15.0	2.56	42.5	6.09	67.5	8.95	92.5	11.70
17.5	2.87	45.0	6.37	70.0	9.15	95.0	11.85
20.0	3.29	47.5	6.59	72.5	9.37	97.5	11.92
22.5	3.78	50.0	6.80	75.0	9.62	100.0	11.98
25.0	4.10						

APPENDIX A-12

Aqueous tension of water at different temperatures

Temperature °C	*Aqueous tension (mm Hg)*	*Temperature °C*	*Aqueous tension (mm Hg)*
20	17.54	28	28.35
21	18.65	29	30.04
22	19.83	30	31.82
23	21.07	31	33.68
24	22.36	32	35.66
25	23.75	33	37.63
26	25.20	34	39.90
27	26.75	35	42.18

APPENDIX A—13

Appendix - Data of Physical Constants of Some Aqueous solutions at different concentrations.

ACETIC ACID. CH_3COOH

MOLECULAR WEIGHT = 60.05
RELATIVE SPECIFIC REFRACTIVITY - 1.065

A % by wt.	ρ D_4^{20}	D_{20}^{20}	C_s g/l	M g-mol/l	C_w g/l	$(C_s - C_w)$ g/l	$(n - n_w)$ × 10^4	n	Δ °C	O Os/kg	S g-mol/l	η η/η_w	ν cS	φ rhe	γ mmho/cm	T g-mol/l
0.00	0.9982	1.0000	0.0	0,000	998.2	0.0	0	1.3330	0.000	0.000	0.000	1.000	1.004	99.80	0.0	0.000
0.50	0.9989	1.0007	5.0	0,083	993.9	4.3	4	1.3334	0.159	0.086	0.045	1.010	1.013	98.81	0.3	0.003
1.00	0.9996	1.0014	10.0	0,166	989.6	8.6	7	1.3337	0.317	0.170	0.091	1.020	1.022	97.84	0.6	0.006
1.50	1.0003	1.0021	15.0	0,250	985.3	12.9	11	1.3341	0.474	0.255	0.137	1.030	1.032	96.90	0.7	0.007
2.00	1.0011	1.0028	20.0	0,333	981.0	17.2	15	1.3345	0.630	0.339	0.183	1.040	1.041	95.96	0.8	0.008
2.50	1.0018	1.0035	25.0	0,417	976.7	21.5	18	1.3348	0.786	0.423	0.229	1.050	1.051	95.02	0.9	0.009
3.00	1.0025	1.0042	30.1	0,501	972.4	25.9	22	1.3352	0.942	0.507	0.275	1.061	1.060	94.07	1.0	0.010
3.50	1.0031	1.0049	35.1	0,585	968.0	30.2	26	1.3355	1.099	0.591	0.321	1.072	1.070	93.14	1.1	0.010
4.00	1.0038	1.0056	40,2	0,669	963.7	34.5	29	1.3359	1.256	0.675	0.367	1.082	1.080	92.24	1.1	0.011
4.50	1.0045	1.0063	45,2	0,753	959.3	38.9	33	1.3363	1.415	0.761	0.414	1.092	1.090	91.36	1.2	0.011
5.00	1.0052	1.0070	50.3	0,837	955.0	43.3	36	1.3366	1.576	0.847	0.461	1.103	1.099	90.50	1.2	0.012
5.50	1.0059	1.0077	55,3	0,921	950.6	47.6	40	1.3370	1.737	0.934	0.508	1.113	1.109	89.66	1.3	0.012
6.00	1.0066	1.0084	60,4	1,006	946.2	52.0	44	1.3373	1.899	1.021	0.555	1.123	1.118	88.87	1.3	0.013
6.50	1.0073	1.0091	65,5	1,090	941.8	56.4	47	1.3377	2.062	1.108	0.602	1.132	1.126	88.14	1.4	0.013
7.00	1.0080	1.0098	70,6	1,175	937.4	60.8	51	1.3381	2.225	1.196	0.650	1.141	1.134	87.46	1.4	0.013
7.50	1.0087	1.0105	75,7	1,260	933.0	65.2	54	1.3384	2.390	1.285	0.697	1.150	1.142	86.78	1.4	0.014
8.00	1.0093	1.0111	80,7	1,345	928.6	69.6	58	1.3388	2.555	1.374	0.745	1.160	1.152	86.03	1.4	0.014
8.50	1.0100	1.0118	85,9	1,430	924.2	74.1	62	1.3391	2.722	1.463	0.792	1.171	1.162	85.20	1.5	0.014
9.00	1.0107	1.0125	91,0	1,515	919.7	78.5	65	1.3395	2.889	1.553	0.840	1.184	1.173	84.31	1.5	0.014
9.50	1.0114	1.0132	96,1	1,600	915,3	82.9	69	1.3399	3.057	1.644	0.888	1.196	1.185	83.43	1.5	0.015
10.00	1.0121	1.0138	101,2	1,685	910,8	87.4	72	1.3402	3.226	1.734	0.935	1.208	1.196	82.62	1.5	0.015
11.00	1.0134	1.0152	111,5	1,856	901,9	96,4	79	1.3409	3.567	1.918	1.031	1.229	1.215	81.19	1.6	0.015
12.00	1.0147	1.0165	121,8	2,028	893,0	105,3	86	1.3416	3.911	2.103	1.127	1.250	1.234	79.84	1.6	0.016
13.00	1.0161	1.0178	132,1	2,200	884,0	114,3	93	1.3423	4.259	2.290	1.223	1.272	1.255	78.43	1.6	0.016
14.00	1.0174	1.0192	142,4	2,372	874,9	123,3	100	1.3430	4.611	2.479	1.320	1.295	1.275	77.07	1.7	0.016
15.00	1.0187	1.0205	152,8	2,545	865,9	132.4	107	1.3437	4.967	2.670	1.415	1.317	1.295	75.79	1.7	0.016
16.00	1.0200	1.0218	163,2	2,718	856,8	141.5	114	1.3444	5.33	2.86	1.511	1.338	1.314	74.59	1.7	0.015
17.00	1.0213	1.0231	173,6	2,891	847,6	150,6	121	1.3451	5.69	3.06	1.607	1.357	1.331	73.54	1.7	0.017
18.00	1.0225	1.0243	184,1	3,065	838,5	159.8	128	1.3458	6.06	3.26	1.703	1.377	1.349	72.48	1.7	0.017
19.00	1.0238	1.0256	194,5	3,239	829,3	169,0	135	1.3465	6.43	3.46	1.798	1.402	1.372	71.18	1.7	0.017

20.00	1,0250	1.0269	205,0	3,414	820,0	178.2	142	1.3472	[illegible]	3.66	1.894	1.428	1.396	69.89	1.7	0.017
22.00	1.0275	1.0293	226,1	3,764	801,5	196.8	155	1.3485	7.57	4.07	2.084	1.475	1.438	67.66	1.7	0.017
24.00	1.0299	1.0318	247,2	4,116	782,8	215.5	169	1.3498	8.36	4.49	2.273	1.522	1.481	65.57	1.7	0.016
26.00	1,0323	1.0341	268,4	4,470	763,9	234.4	182	1.3512	9.17	4.93	2.462	1.569	1.523	63.61	1.6	0.015
28.00	1,0346	1.0365	289,7	4,823	744,9	253,3	195	1.3525	10.00	5.38	2.650	1.610	1.555	61.99	1.5	0.015
30.00	1,0369	1.0388	311,1	5,180	725,8	272,4	207	1.3537	10.84	5.83	2.835	1.666	1.610	59.90	1.4	0.014
32.00	1,0391	1.0410	332,5	5,537	706,6	291.6	220	1.3550	11.70	6.29	3.017	1.712	1.651	58.29	1.4	0.013
34.00	1,0413	1.0431	354,0	5.896	687,3	311.0	232	1.3562	12.55	6.75	3.192	1.758	1.692	56.77	1.3	0.012
36.00	1,0434	1.0452	375,6	6.255	667,8	330.5	245	1.3574	13.38	7.20	3.359	1.808	1.736	55.20	1.2	0.011
38.00	1,0454	1.0473	397,3	6.615	648.2	350.1	257	1.3586				1.848	1.771	54.00	1.1	0.011
40.00	1,0474	1.0492	419,0	6.977	628,4	369.8	268	1.3598				1.908	1.825	52.31	1.1	0.010
42.00	1,0493	1.0511	440,7	7.339	608,6	389.7	280	1.3610				1.956	1.868	51.02	1.0	0.010
44.00	1,0510	1.0529	462,3	7.701	588,6	409.7	291	1.3621				2.003	1.910	49.83	1.0	0.009
46.00	1,0528	1.0547	484 3	8.065	568,5	429.7	302	1.3632				2.048	1.949	48.73	0.9	0.009
48.00	1,0545	1.0564	506 2	8.429	548.4	449.9	312	1.3642				2.106	2.001	47.39	0.8	0.008
50.00	1,0562	1.0581	528 1	8.794	528.1	470.1	323	1.3653				2.154	2.043	46.33	0.8	0.007
52.00	1,0577	1.0596	550 0	9.159	507.7	490.5	333	1.3663				2.208	2.092	45.20	0.7	0.007
54.00	1,0592	1.0611	572 0	9.525	487.2	511.0	343	1.3673				2.260	2.138	44.16	0.7	0.006
56.00	1,0605	1.0624	593.9	9.890	466.6	531.6	352	1.3682				2.303	2.176	43.33	0.5	0.005
58.00	1,0618	1.0636	615.8	10.255	445.9	552.3	361	1.3691				2.355	2.222	42.38	0.3	0.003
60.00	1,0629	1.0648	637.7	10.620	425.2	573.1	370	1.3700				2.404	2.266	41.51	0.4	0.004
62.00	1,0640	1.0659	659.7	10.985	404.3	593.9	378	1.3708				2.451	2.308	40.72		
64.00	1,0650	1.0668	681.6	11.350	383.4	614.8	386	1.3716				2.497	2.349	39.97		
66.00	1,0659	1.0678	703.5	11.715	362.4	635.8	394	1.3724				2.548	2.395	39.17		
68.00	1,0668	1.0687	725.4	12.080	341.4	656.9	402	1.3712				2.589	2.432	38.55		
70.00	1,0673	1.0692	747.1	12.441	320.2	678.0	409	1.3738				2.624	2.463	38.03		
72.00	1,0676	1.0695	768.7	12.800	298.9	699.3	415	1.3745				2.657	2.494	37.56		
74.00	1,0678	1.0697	790.2	13.158	277.6	720.6	421	1.3751				2.682	2.517	37.21		
76.00	1,0680	1.0699	811.7	13.516	256.3	741.9	427	1.3757				2.709	2.542	36.84		
78.00	1,0681	1.0700	833.1	13.956	235.0	763.2	432	1.3762				2.715	2.547	36.76		
80.00	1,0680	1.0699	854.4	14.227	213.6	784.6	437	1.3767				2.715	2.547	36.76		
82.00	1,0677	1.0696	875.5	14.579	192.2	806.0	441	1.3770				2.691	2.525	37.09		
84.00	1,0673	1.0692	896.5	14.928	170.8	827.4	443	1.3773				2.653	2.491	37.62		
86.00	1,0666	1.0685	917.3	15.275	149.3	848.9	444	1.3774				2.591	2.434	38.52		
88.00	1,0658	1.0677	937.9	15.618	127.9	870.3	444	1.3774				2.506	2.356	39.82		
90.00	1,0644	1.0663	958.0	15.953	106.4	891.8	441	1.3771				2.381	2.241	41.92		
92.00	1,0629	1.0648	977.9	16.284	85.0	913.2	436	1.3766				2.236	2.108	44.63		
94.00	1,0606	1.0625	997.0	16.602	63.6	934.6	429	1.3759				2.032	1.920	49.11		
96.00	1,0578	1.0597	1015.5	16.912	42.3	955.9	418	1.3748				1.809	1.714	55.17		
98.00	1,0538	1,0557	1032.7	17.196	21.1	977.1	404	1.3734				1.532	1.457	65.14		
100.00	1.0477	1.0496	1047.7	17.446	0.0	998.2	386	1.3716				1.221	1.168	81.73		

D-GLUCOSE (DEXTROSE), $C_6H_{12}O_6 \cdot 1H_2O$

MOLECULAR WEIGHT = 180.16   FORMULA WEIGHT, HYDRATE = 198.17
RELATIVE SPECIFIC REFRACTIVITY = 1.031

A% by wt.	H% by wt.	ρ D_4^{20}	D_{20}^{20}	C_s g/l	M g-mol/l	C_w g/l	$(C_o - C_w)$ g/l	$(n - n_o)$ $\times 10^4$	n	Δ °C	O Os/kg	S g-mol/l	η/η_o	η/ρ cS	ϕ rhe	γ mmho/cm	T g-mol/l
0.50	0.55	1.0001	1.0019	5.0	0.028	995.1	3.1	7	1.3337	0.047	0.025	0.013	1.008	1.010	99.01		
1.00	1.10	1.0020	1.0038	10.0	0.056	992.0	6.2	14	1.3344	0.107	0.057	0.030	1.019	1.019	97.94		
1.50	1.65	1.0039	1.0057	15.1	0.084	988.9	9.4	21	1.3351	0.158	0.085	0.045	1.034	1.032	96.54		
2.00	2.20	1.0058	1.0076	20.1	0.112	985.7	12.5	28	1.3358	0.214	0.115	0.061	1.050	1.046	95.05		
2.50	2.75	1.0078	1.0095	25.2	0.140	982.6	15.7	36	1.3366	0.270	0.145	0.077	1.065	1.059	93.68		
3.00	3.30	1.0097	1.0115	30.3	0.168	979.4	18.8	43	1.3373	0.323	0.174	0.093	1.081	1.072	92.36		
3.50	3.85	1.0116	1.0134	35.4	0.197	976.2	22.0	50	1.3380	0.377	0.202	0.108	1.096	1.085	91.08		
4.00	4.40	1.0136	1.0154	40.5	0.225	973.0	25.2	57	1.3387	0.433	0.233	0.125	1.111	1.098	89.82		
4.50	4.95	1.0155	1.0173	45.7	0.254	969.8	28.4	65	1.3395	0.490	0.264	0.142	1.127	1.112	88.57		
5.00	5.50	1.0175	1.0191	50.9	0.282	966.6	31.6	72	1.3402	0.549	0.295	0.159	1.143	1.126	87.31		
5.50	6.05	1.0194	1.0212	56.1	0.311	963.4	34.9	79	1.3409	0.608	0.327	0.176	1.160	1.140	86.06		
6.00	6.60	1.0214	1.0232	61.3	0.340	960.1	38.1	87	1.3417	0.668	0.359	0.194	1.177	1.154	84.82		
6.50	7.15	1.0234	1.0252	66.5	0.369	956.9	41.4	94	1.3424	0.729	0.392	0.212	1.194	1.169	83.59		
7.00	7.70	1.0254	1.0272	71.8	0.398	953.6	44.6	102	1.3432	0.790	0.425	0.230	1.212	1.184	82.37		
7.50	8.25	1.0274	1.0292	77.1	0.428	950.3	47.9	109	1.3439	0.851	0.458	0.248	1.230	1.199	81.17		
8.00	8.80	1.0294	1.0312	82.4	0.457	947.0	51.2	117	1.3447	0.913	0.491	0.266	1.248	1.215	79.97		
8.50	9.35	1.0314	1.0332	87.7	0.487	943.7	54.5	124	1.3454	0.975	0.524	0.284	1.267	1.231	78.77		
9.00	9.90	1.0334	1.0352	93.0	0.516	940.4	57.8	132	1.3462	1.038	0.558	0.303	1.286	1.247	77.58		
9.50	10.45	1.0354	1.0373	98.4	0.546	937.1	61.2	139	1.3469	1.102	0.592	0.322	1.306	1.264	76.39		
10.00	11.00	1.0375	1.0393	103.7	0.576	933.7	64.5	147	1.3477	1.167	0.627	0.341	1.327	1.282	75.21		
11.00	12.10	1.0416	1.0434	114.6	0.636	927.0	71.2	162	1.3492	1.303	0.700	0.381	1.369	1.317	72.89		
12.00	13.20	1.0457	1.0475	125.5	0.697	920.2	78.0	178	1.3508	1.443	0.776	0.422	1.413	1.354	70.63		
13.00	14.30	1.0498	1.0517	136.5	0.758	913.4	84.9	193	1.3523	1.586	0.853	0.464	1.459	1.393	68.40		
14.00	15.40	1.0540	1.0559	147.6	0.819	906.4	91.8	209	1.3539	1.731	0.931	0.506	1.509	1.434	66.15		
15.00	16.50	1.0582	1.0601	158.7	0.881	899.5	98.8	225	1.3555	1.880	1.011	0.550	1.563	1.480	63.85		
16.00	17.60	1.0624	1.0643	170.0	0.944	892.5	105.8	241	1.3571	2.033	1.093	0.594	1.622	1.530	61.53		
17.00	18.70	1.0667	1.0686	181.3	1.007	885.4	112.9	257	1.3587	2.190	1.178	0.640	1.685	1.583	59.21		
18.00	19.80	1.0710	1.0729	192.8	1.070	878.2	120.0	273	1.3603	2.353	1.265	0.687	1.753	1.640	56.93		
19.00	20.90	1.0753	1.0772	204.3	1.134	871.0	127.2	289	1.3619	2.521	1.355	0.735	1.825	1.700	54.70		
20.00	22.00	1.0797	1.0816	215.9	1.199	863.7	134.5	306	1.3635	2.696	1.449	0.785	1.900	1.763	52.53		
22.00	24.20	1.0884	1.0904	239.5	1.329	849.0	149.1	339	1.3668	3.073	1.652	0.892	2.059	1.896	48.47		
24.00	26.40	1.0973	1.0993	263.4	1.462	834.0	164.3	372	1.3702	3.480	1.871	1.007	2.238	2.044	44.59		
26.00	28.60	1.1063	1.1083	287.6	1.597	818.7	179.6	406	1.3736	3.900	2.097	1.124	2.453	2.222	40.69		
28.00	30.80	1.1154	1.1174	312.3	1.734	803.1	195.1	440	1.3770	4.337	2.332	1.244	2.702	2.427	36.94		

30.00	33.00	1.1246	1.1266	337.4	1.871	787.2	211.0	475	1.3805	4.794	2.577	1.369	2.992	2.666	33.36
32.00	35.20	1.1340	1.1360	362.9	2.014	771.1	227.1	511	1.3840				3.317	2.931	30.09
34.00	37.40	1.1434	1.1454	388.8	2.158	754.6	243.6	546	1.3876				3.697	3.240	26.99
36.00	39.60	1.1529	1.1550	415.1	2.304	737.9	260.3	582	1.3912				4.185	3.637	23.85
38.00	41.80	1.1626	1.1647	441.9	2.452	720.8	277.4	619	1.3949				4.776	4.116	20.90
40.00	44.00	1.1724	1.1745	469.0	2.601	703.5	294.8	656	1.3986				5.482	4.685	18.21
42.00	46.20	1.1823	1.1844	496.6	2.756	685.3	312.5	694	1.4024				6.275	5.318	15.90
44.00	48.40	1.1924	1.1945	524.7	2.912	667.7	330.5	732	1.4062				7.221	6.068	13.82
46.00	50.60	1.2026	1.2047	553.2	3.071	649.4	348.8	771	1.4101				8.437	7.029	11.83
48.00	52.80	1.2130	1.2151	582.2	3.232	630.7	367.5	811	1.4141				9.863	8.148	10.12
50.00	55.00	1.2235	1.2257	611.7	3.396	611.7	386.5	851	1.4181				11.86	9.713	8.41
52.00	57.20	1.2342	1.2364	641.8	3.562	592.4	405.8	892	1.4222				14.46	11.74	6.90
54.00	59.40	1.2451	1.2473	672.4	3.732	572.8	425.5	933	1.4263				17.88	14.39	5.58
56.00	61.60	1.2562	1.2585	703.5	3.905	552.7	445.5	976	1.4306				22.84	18.22	4.37
58.00	63.80	1.2676	1.2699	735.2	4.081	532.4	465.8	1020	1.4349				29.33	23.18	3.40
60.00	66.00	1.2793	1.2816	767.6	4.261	511.7	486.5	1064	1.4394				37.37	29.27	2.67

GLYCEROL, $CH_2OHCHOHCH_2OH$

MOLECULAR WEIGHT = 92.09
RELATIVE SPECIFIC REFRACTIVITY = 1.109

A*, by wt.	ρ D_4^{20}	D_{20}^{20}	C_s g/l	M g-mol/l	C_w g/l	$(C_o - C_w)$ g/l	$(n - n_o)$ × 10^4	n	Δ °C	O Os/kg	S g-mol/l	η/η_o	η/ρ cS	φ rhe	mmho/cm	T g-mol/l
0.50	0.9994	1.0011	5.0	0.054	994.4	3.9	6	1.3336	0.072	0.039	0.020	1.009	1.012	98.89		
1.00	1.0005	1.0023	10.0	0.109	990.5	7.7	12	1.3342	0.180	0.097	0.051	1.020	1.022	97.84		
2.00	1.0028	1.0046	20.1	0.218	982.7	15.5	23	1.3353	0.411	0.221	0.119	1.046	1.045	95.41		
3.00	1.0051	1.0069	30.2	0.327	974.9	23.3	35	1.3365	0.627	0.337	0.182	1.072	1.068	93.12		
4.00	1.0074	1.0092	40.3	0.438	967.1	31.2	46	1.3376	0.849	0.456	0.247	1.098	1.092	90.93		

GLYCEROL, $CH_2OHCHOHCH_2OH$—(Continued)

A% by wt.	ρ D_4^{20}	D_{20}^{20}	C_s g/l	M g-mol/l	C_w g/l	$(C_w^\circ - C_w)$ g/l	$(n - n_0)$ × 10^4	n	Δ °C	O Os/kg	S g-mol/l	η/η_0	η/ρ cS	φ rhe	mmho/cm	T g-mol/l
5.00	1.0097	1.0115	50.5	0.548	959.2	39.0	58	1.3388	1.078	0.580	0.315	1.125	1.116	88.71		
6.00	1.0120	1.0138	60.7	0.659	951.3	46.9	70	1.3400	1.316	0.708	0.385	1.155	1.143	86.44		
7.00	1.0144	1.0162	71.0	0.771	943.4	54.9	82	1.3412	1.561	0.839	0.457	1.186	1.171	84.17		
8.00	1.0167	1.0185	81.3	0.883	935.4	62.9	94	1.3424	1.811	0.974	0.530	1.218	1.201	81.90		
9.00	1.0191	1.0209	91.7	0.996	927.4	70.9	106	1.3436	2.064	1.110	0.603	1.253	1.232	79.67		
10.00	1.0215	1.0233	102.1	1.109	919.3	78.9	118	1.3448	2.323	1.249	0.678	1.288	1.263	77.48		
12.00	1.0262	1.0281	123.1	1.337	903.1	95.1	142	1.3472	2.880	1.548	0.837	1.362	1.330	73.28		
14.00	1.0311	1.0329	144.4	1.568	886.7	111.5	167	1.3496	3.469	1.865	1.004	1.442	1.401	69.22		
16.00	1.0360	1.0378	165.8	1.800	870.2	128.0	191	1.3521	4.094	2.201	1.177	1.530	1.480	65.22		
18.00	1.0409	1.0428	187.4	2.035	853.6	144.7	217	1.3547	4.756	2.557	1.359	1.627	1.566	61.34		
20.00	1.0459	1.0478	209.2	2.272	836.8	161.5	242	1.3572	5.46	2.93	1.546	1.734	1.661	57.56		
24.00	1.0561	1.0580	253.5	2.752	802.6	195.6	294	1.3624	7.01	3.77	1.944	1.984	1.882	50.31		
28.00	1.0664	1.0683	298.6	3.243	767.8	230.4	347	1.3676	8.77	4.71	2.370	2.274	2.136	43.89		
32.00	1.0770	1.0789	344.6	3.742	732.3	265.9	400	1.3730	10.74	5.78	2.814	2.632	2.449	37.91		
36.00	1.0876	1.0896	391.5	4.252	696.1	302.2	455	1.3785	12.96	6.97	3.276	3.082	2.839	32.38		
40.00	1.0984	1.1003	439.4	4.771	659.0	339.2	511	1.3841	15.50	8.33	3.757	3.646	3.326	27.37		
44.00	1.1092	1.1112	488.1	5.300	621.2	377.1	567	1.3897				4.434	4.005	22.51		
48.00	1.1200	1.1220	537.6	5.838	582.4	415.8	624	1.3954				5.402	4.833	18.47		
52.00	1.1308	1.1328	588.0	6.385	542.8	455.4	681	1.4011				6.653	5.895	15.00		
56.00	1.1419	1.1439	639.4	6.944	502.4	495.8	739	1.4069				8.332	7.311	11.98		
60.00	1.1530	1.1551	691.8	7.513	461.2	537.0	799	1.4129				10.66	9.264	9.36		
64.00	1.1643	1.1663	745.1	8.091	419.1	579.1	859	1.4189				13.63	11.73	7.32		
68.00	1.1755	1.1775	799.3	8.680	376.1	622.1	919	1.4249				18.42	15.70	5.42		
72.00	1.1866	1.1887	854.3	9.277	332.2	666.0	980	1.4310				27.57	23.28	3.62		
76.00	1.1976	1.1997	910.2	9.883	287.4	710.8	1040	1.4370				40.49	33.88	2.46		
80.00	1.2085	1.2106	966.8	10.498	241.7	756.5	1101	1.4431				59.78	49.57	1.67		
84.00	1.2192	1.2214	1024.2	11.121	195.1	803.2	1162	1.4492				84.17	69.18	1.19		
88.00	1.2299	1.2320	1082.3	11.752	147.6	850.7	1223	1.4553				147.2	119.9	0.68		
92.00	1.2404	1.2426	1141.1	12.392	99.2	899.0	1284	1.4613				383.7	310.0	0.26		
96.00	1.2508	1.2530	1200.7	13.039	50.0	948.2	1344	1.4674				778.9	624.0	0.13		
100.00	1.2611	1.2633	1261.1	13.694	0.0	998.2	1405	1.4735				1759.6	1398.1	0.06		

HYDROCHLORIC ACID, HCl

MOLECULAR WEIGHT = 36.47
RELATIVE SPECIFIC REFRACTIVITY = 1.152

A% by wt.	ρ D_4^{20}	D_{20}^{20}	C_s g/l	M g-mol/l	C_w g/l	$(C_o - C_w)$ g/l	$(n - n_o) \times 10^4$	n	Δ °C	O Os/kg	S g-mol/l	η/η_o	η/ρ cS	φ rhe	mmho/cm	T g-mol/l
0.50	1.0007	1.0025	5.0	0.137	995.7	2.5	12	1.3341	0.486	0.261	0.141	1.006	1.008	99.16	45.1	0.537
1.00	1.0031	1.0049	10.0	0.275	993.1	5.1	23	1.3353	0.989	0.532	0.289	1.013	1.012	98.50	92.9	1.23
1.50	1.0056	1.0074	15.1	0.414	990.5	7.7	35	1.3365	1.519	0.817	0.444	1.020	1.016	97.84	140.	2.10
2.00	1.0081	1.0098	20.2	0.553	987.9	10.3	46	1.3376	2.076	1.116	0.607	1.027	1.021	97.17	183.	3.14
2.50	1.0105	1.0123	25.3	0.693	985.3	13.0	58	1.3388	2.662	1.431	0.775	1.034	1.026	96.49	220.	4.85
3.00	1.0130	1.0148	30.4	0.833	982.6	15.6	69	1.3399	3.276	1.761	0.949	1.042	1.030	95.81		
3.50	1.0154	1.0172	35.5	0.975	979.9	18.3	81	1.3411	3.916	2.105	1.128	1.049	1.035	95.12		
4.00	1.0179	1.0197	40.7	1.116	977.2	21.0	92	1.3422	4.579	2.462	1.311	1.057	1.040	94.43		
4.50	1.0204	1.0222	45.9	1.259	974.4	23.8	104	1.3434	5.27	2.83	1.496	1.065	1.046	93.73		
5.00	1.0228	1.0246	51.1	1.402	971.7	26.5	115	1.3445	5.98	3.22	1.683	1.073	1.051	93.04		
5.50	1.0253	1.0271	56.4	1.546	968.9	29.3	127	1.3457	6.73	3.62	1.874	1.081	1.056	92.34		
6.00	1.0278	1.0296	61.7	1.691	966.1	32.1	138	1.3468	7.52	4.04	2.070	1.089	1.062	91.64		
6.50	1.0302	1.0321	67.0	1.836	963.3	35.0	150	1.3480	8.34	4.49	2.269	1.097	1.067	90.94		
7.00	1.0327	1.0345	72.3	1.982	960.4	37.8	162	1.3491	9.22	4.96	2.474	1.106	1.073	90.24		
7.50	1.0352	1.0370	77.6	2.129	957.5	40.7	173	1.3503	10.14	5.45	2.681	1.115	1.079	89.54		
8.00	1.0377	1.0395	83.0	2.276	954.6	43.6	185	1.3515	11.10	5.97	2.890	1.123	1.085	88.85		
8.50	1.0401	1.0420	88.4	2.424	951.7	46.5	196	1.3526	12.10	6.51	3.101	1.132	1.091	88.15		
9.00	1.0426	1.0445	93.8	2.573	948.8	49.5	208	1.3538	13.15	7.07	3.313	1.141	1.097	87.46		
9.50	1.0451	1.0469	99.3	2.722	945.8	52.4	219	1.3549	14.25	7.66	3.526	1.150	1.103	86.77		
10.00	1.0476	1.0494	104.8	2.872	942.8	55.4	231	1.3561	15.40	8.28	3.740	1.159	1.109	86.08		
11.00	1.0526	1.0544	115.8	3.175	936.8	61.4	254	1.3584	17.85	9.60	4.166	1.178	1.122	84.71		
12.00	1.0576	1.0594	126.9	3.480	930.7	67.6	277	1.3607	20.51	11.03	4.590	1.197	1.134	83.36		
13.00	1.0626	1.0645	138.1	3.788	924.4	73.8	300	1.3630				1.217	1.148	82.01		
14.00	1.0676	1.0695	149.5	4.098	918.1	80.1	323	1.3653				1.237	1.161	80.68		
15.00	1.0726	1.0745	160.9	4.412	911.8	86.5	347	1.3676				1.258	1.175	79.35		
16.00	1.0777	1.0796	172.4	4.728	905.3	93.0	370	1.3700				1.279	1.189	78.03		
17.00	1.0828	1.0847	184.1	5.047	898.7	99.5	393	1.3723				1.301	1.204	76.72		
18.00	1.0878	1.0898	195.8	5.369	892.0	106.2	416	1.3746				1.323	1.219	75.42		
19.00	1.0929	1.0949	207.7	5.694	885.3	113.0	439	1.3769				1.347	1.235	74.11		
20.00	1.0980	1.1000	219.6	6.022	878.4	119.8	462	1.3792				1.371	1.251	72.80		
22.00	1.1083	1.1102	243.8	6.686	864.5	133.8	509	1.3838				1.423	1.286	70.15		
24.00	1.1185	1.1205	268.4	7.361	850.1	148.1	555	1.3884				1.480	1.326	67.44		
26.00	1.1288	1.1308	293.5	8.047	835.3	162.9	600	1.3930				1.544	1.371	64.63		
28.00	1.1391	1.1411	318.9	8.745	820.1	178.1	646	1.3976				1.617	1.423	61.71		

30.00	1.1492	1.1513	344.8	9.454	804.5	193.8	691	1.4020	1.702	1.484	58.64
32.00	1.1594	1.1614	371.0	10.173	788.4	209.9	736	1.4066	1.795	1.551	55.61
34.00	1.1693	1.1714	397.6	10.901	771.8	226.5	782	1.4112	1.896	1.625	52.63
36.00	1.1791	1.1812	424.5	11.639	754.6	243.6	828	1.4158	1.998	1.698	49.55
38.00	1.1886	1.1907	451.7	12.385	736.9	261.3	874	1.4204	2.101	1.771	47.51
40.00	1.1977	1.1999	479.1	13.137	718.6	279.6	920	1.4250			

SODIUM CARBONATE, $Na_2CO_3 \cdot 10H_2O$

MOLECULAR WEIGHT = 106.00 FORMULA WEIGHT, HYDRATE = 286.16
RELATIVE SPECIFIC REFRACTIVITY = 0.619

A % by wt.	H % by wt.	ρ D_4^{20}	D_{20}^{20}	C_s g/l	M g-mol/l	C_w g/l	$(C_w^0 - C_w)$ g/l	$(n - n_0) \times 10^4$	n	Δ °C	O Os/kg	S g-mol/l	η/η_0	η/ρ cS	φ rhe	γ mmho/cm	T g-mol/l
0.50	1.35	1.0034	1.0052	5.0	0.047	998.4	−0.2	11	1.3341	0.222	0.119	0.063	1.023	1.021	97.58	7.0	0.072
1.00	2.70	1.0086	1.0104	10.1	0.095	998.5	−0.3	23	1.3352	0.425	0.229	0.123	1.047	1.040	95.32	13.1	0.139
1.50	4.05	1.0138	1.0156	15.2	0.143	998.6	−0.4	34	1.3364	0.598	0.322	0.174	1.073	1.060	93.03	18.4	0.201
2.00	5.40	1.0190	1.0208	20.4	0.192	998.6	−0.4	45	1.3375	0.751	0.404	0.219	1.100	1.082	90.73	23.3	0.260
2.50	6.75	1.0242	1.0260	25.6	0.242	998.6	−0.4	56	1.3386	0.915	0.492	0.267	1.128	1.104	88.46	27.8	0.316
3.00	8.10	1.0294	1.0312	30.9	0.291	998.5	−0.3	67	1.3397	1.082	0.582	0.316	1.157	1.127	86.23	32.0	0.369
3.50	9.45	1.0346	1.0364	36.2	0.342	998.4	−0.2	78	1.3408	1.250	0.672	0.365	1.188	1.150	84.01	36.0	0.420
4.00	10.80	1.0398	1.0416	41.6	0.392	998.2	0.0	89	1.3419	1.421	0.764	0.416	1.220	1.176	81.81	39.8	0.468
4.50	12.15	1.0450	1.0468	47.0	0.444	998.0	0.3	100	1.3430	1.593	0.857	0.466	1.253	1.202	79.62	43.5	0.515
5.00	13.50	1.0502	1.0521	52.5	0.495	997.7	0.5	110	1.3440	1.768	0.951	0.517	1.289	1.230	77.42	47.0	0.562
5.50	14.85	1.0554	1.0573	58.0	0.548	997.3	0.9	121	1.3451	1.945	1.046	0.569	1.326	1.259	75.26	50.4	0.608
6.00	16.20	1.0606	1.0625	63.6	0.600	997.0	1.3	132	1.3462	2.125	1.142	0.621	1.364	1.289	73.16	53.6	0.652
6.50	17.55	1.0658	1.0677	69.3	0.654	996.5	1.7	142	1.3472				1.404	1.320	71.09	56.7	0.694
7.00	18.90	1.0711	1.0730	75.0	0.707	996.1	2.1	153	1.3483				1.445	1.352	69.05	59.7	0.735
7.50	20.25	1.0763	1.0782	80.7	0.762	995.6	2.6	164	1.3494				1.489	1.386	67.04	62.4	0.774
8.00	21.60	1.0816	1.0835	86.5	0.816	995.1	3.1	174	1.3504				1.535	1.422	65.03	65.1	0.812
8.50	22.95	1.0869	1.0888	92.4	0.872	994.5	3.7	185	1.3515				1.583	1.460	63.03	67.6	0.848
9.00	24.30	1.0922	1.0942	98.3	0.927	993.9	4.3	196	1.3525				1.635	1.500	61.03	70.0	0.883
9.50	25.65	1.0975	1.0995	104.3	0.984	993.3	5.0	206	1.3536				1.691	1.543	59.03	72.2	0.916
10.00	27.00	1.1029	1.1048	110.3	1.040	992.6	5.6	217	1.3547				1.750	1.590	57.03	74.4	0.948
11.00	29.70	1.1136	1.1156	122.5	1.156	991.1	7.1	238	1.3568				1.880	1.691	53.09	78.3	1.00
12.00	32.40	1.1244	1.1264	134.9	1.273	989.5	8.8	259	1.3589				2.024	1.803	49.32	81.7	1.05
13.00	35.10	1.1353	1.1373	147.6	1.392	987.7	10.5	280	1.3610				2.182	1.926	45.74	84.6	1.10
14.00	37.79	1.1463	1.1483	160.5	1.514	985.8	12.4	301	1.3631				2.356	2.059	42.36	86.9	1.14
15.00	40.49	1.1574	1.1595	173.6	1.638	983.8	14.4	322	1.3652				2.546	2.204	39.20	88.6	1.16

SODIUM CHLORIDE, NaCl

MOLECULAR WEIGHT = 58.44
RELATIVE SPECIFIC REFRACTIVITY = 0.794

A % by wt.	ρ D_4^{20}	D_{20}^{20}	C_s g/l	M g-mol/l	C_w g/l	$(C_o - C_w)$ g/l	$(n - n_o) \times 10^4$	n	Δ °C	O Os/kg	S g-mol/l	η/η_o	η/ρ cS	φ rhe	γ mmho/cm	T g-mol/l
0.10	0.9989	1.0007	1.0	0.017	997.9	0.3	2	1.3332	0.062	0.033	0.017	1.002	1.005	99.61	1.7	0.017
0.20	0.9997	1.0014	2.0	0.034	997.7	0.6	4	1.3333	0.121	0.065	0.034	1.004	1.006	99.43	3.3	0.034
0.30	1.0004	1.0021	3.0	0.051	997.4	0.9	5	1.3335	0.181	0.097	0.051	1.006	1.007	99.24	5.0	0.051
0.40	1.0011	1.0028	4.0	0.069	997.1	1.2	7	1.3337	0.240	0.129	0.069	1.007	1.008	99.06	6.6	0.069
0.50	1.0018	1.0036	5.0	0.086	996.8	1.5	9	1.3339	0.299	0.161	0.086	1.009	1.009	98.89	8.2	0.086
0.60	1.0025	1.0043	6.0	0.103	996.5	1.8	11	1.3340	0.358	0.192	0.103	1.011	1.011	98.71	9.8	0.103
0.70	1.0032	1.0050	7.0	0.120	996.2	2.1	12	1.3342	0.417	0.224	0.120	1.013	1.012	98.54	11.4	0.120
0.80	1.0039	1.0057	8.0	0.137	995.9	2.4	14	1.3344	0.475	0.256	0.137	1.015	1.013	98.37	12.9	0.137
0.90	1.0046	1.0064	9.0	0.155	995.6	2.7	16	1.3346	0.534	0.287	0.155	1.016	1.014	98.20	14.4	0.155
1.00	1.0053	1.0071	10.1	0.172	995.3	3.0	18	1.3347	0.593	0.319	0.172	1.018	1.015	98.04	16.0	0.172
1.10	1.0060	1.0078	11.1	0.189	995.0	3.3	19	1.3349	0.652	0.351	0.189	1.020	1.016	97.87	17.5	0.189
1.20	1.0068	1.0085	12.1	0.207	994.7	3.6	21	1.3351	0.711	0.382	0.207	1.021	1.017	97.72	18.9	0.207
1.30	1.0075	1.0093	13.1	0.224	994.4	3.9	23	1.3353	0.770	0.414	0.224	1.023	1.017	97.56	20.4	0.224
1.40	1.0082	1.0100	14.4	0.241	994.1	4.2	25	1.3354	0.829	0.446	0.241	1.025	1.018	97.41	21.8	0.241
1.50	1.0089	1.0107	15.1	0.259	993.8	4.5	26	1.3356	0.888	0.478	0.259	1.026	1.019	97.26	23.2	0.259
1.60	1.0096	1.0114	16.2	0.276	993.5	4.8	28	1.3358	0.948	0.509	0.276	1.028	1.020	97.11	24.6	0.276
1.70	1.0103	1.0121	17.2	0.294	993.1	5.1	30	1.3360	1.007	0.541	0.294	1.029	1.021	96.96	26.0	0.294
1.80	1.0110	1.0128	18.2	0.311	992.8	5.4	32	1.3362	1.067	0.573	0.311	1.031	1.022	96.82	27.4	0.311
1.90	1.0117	1.0135	19.2	0.329	992.5	5.7	33	1.3363	1.126	0.605	0.329	1.032	1.022	96.67	28.8	0.329
2.00	1.0125	1.0143	20.2	0.346	992.2	6.0	35	1.3365	1.186	0.638	0.346	1.034	1.023	96.52	30.2	0.346
2.10	1.0132	1.0150	21.3	0.364	991.9	6.3	37	1.3367	1.246	0.670	0.364	1.036	1.024	96.37	31.6	0.364
2.20	1.0139	1.0157	22.3	0.382	991.6	6.5	39	1.3369	1.306	0.702	0.382	1.037	1.025	96.22	33.0	0.382
2.30	1.0146	1.0164	23.3	0.399	991.3	7.0	40	1.3370	1.366	0.734	0.399	1.039	1.026	96.07	34.3	0.399
2.40	1.0153	1.0171	24.4	0.418	991.0	7.3	42	1.3372	1.426	0.767	0.418	1.040	1.027	95.93	35.7	0.418
2.50	1.0160	1.0178	25.4	0.435	990.6	7.6	44	1.3374	1.486	0.799	0.435	1.042	1.028	95.78	37.1	0.435
2.60	1.0168	1.0185	26.4	0.452	990.3	7.9	46	1.3376	1.547	0.832	0.452	1.044	1.028	95.64	38.5	0.452
2.70	1.0175	1.0193	27.5	0.470	990.0	8.2	47	1.3377	1.607	0.864	0.470	1.045	1.029	95.49	39.9	0.470
2.80	1.0182	1.0200	28.5	0.488	989.7	8.6	49	1.3379	1.668	0.897	0.488	1.047	1.030	95.35	41.2	0.488
2.90	1.0189	1.0207	29.5	0.505	989.4	8.9	51	1.3381	1.729	0.930	0.505	1.048	1.031	95.21	42.6	0.505
3.00	1.0196	1.0214	30.6	0.523	989.0	9.2	53	1.3383	1.790	0.962	0.523	1.050	1.032	95.06	44.0	0.523
3.10	1.0203	1.0221	31.6	0.541	988.7	9.5	54	1.3384	1.851	0.995	0.541	1.051	1.033	94.92	45.3	0.541
3.20	1.0211	1.0229	32.7	0.559	988.4	9.9	56	1.3386	1.913	1.028	0.559	1.053	1.033	94.78	46.7	0.559

SODIUM CHLORIDE, NaCl—(Continued)

A % by wt.	ρ D_4^{20}	D_{20}^{20}	C_s g/l	M g-mol/l	C_w g/l	$(C_0 - C_w)$ g/l	$(n - n_0) \times 10^4$	n	Δ °C	O Os/kg	S g-mol/l		η/ρ cS	φ rhe	mmho/cm	T g-mol/l
3.30	1.0218	1.0236	33.7	0.577	988.0	10.2	58	1.3388	1.974	1.061	0.577	1.055	1.034	94.64	48.0	0.577
3.40	1.0225	1.0243	34.8	0.595	987.7	10.5	60	1.3390	2.036	1.094	0.595	1.056	1.035	94.50	49.4	0.595
3.50	1.0232	1.0250	35.8	0.613	987.4	10.8	61	1.3391	2.098	1.128	0.613	1.058	1.036	94.35	50.7	0.613
3.60	1.0239	1.0257	36.9	0.631	987.1	11.2	63	1.3393	2.160	1.161	0.631	1.059	1.037	94.21	52.0	0.631
3.70	1.0246	1.0265	37.9	0.649	986.7	11.5	65	1.3395	2.222	1.194	0.649	1.061	1.037	94.07	53.3	0.649
3.80	1.0254	1.0272	39.0	0.667	986.4	11.8	67	1.3397	2.284	1.228	0.667	1.063	1.038	93.93	54.7	0.667
3.90	1.0261	1.0279	40.0	0.685	986.1	12.2	68	1.3398	2.347	1.262	0.685	1.064	1.039	93.78	56.0	0.685
4.00	1.0268	1.0286	41.1	0.703	985.7	12.5	70	1.3400	2.409	1.295	0.703	1.066	1.040	93.64	57.3	0.703
4.10	1.0275	1.0293	42.1	0.721	985.4	12.8	72	1.3402	2.472	1.329	0.721	1.067	1.041	93.49	58.6	0.721
4.20	1.0282	1.0301	43.2	0.739	985.1	13.2	74	1.3404	2.535	1.363	0.739	1.069	1.042	93.35	59.9	0.739
4.30	1.0290	1.0308	44.2	0.757	984.7	13.5	75	1.3405	2.598	1.397	0.757	1.071	1.043	93.20	61.2	0.757
4.40	1.0297	1.0315	45.3	0.775	984.4	13.9	77	1.3407	2.662	1.431	0.775	1.072	1.044	93.06	62.5	0.775
4.50	1.0304	1.0322	46.4	0.794	984.0	14.2	79	1.3409	2.725	1.465	0.794	1.074	1.045	92.91	63.8	0.794
4.60	1.0311	1.0330	47.4	0.812	983.7	14.5	81	1.3411	2.789	1.500	0.812	1.076	1.046	92.76	65.1	0.812
4.70	1.0318	1.0337	48.5	0.830	983.4	14.9	82	1.3412	2.853	1.534	0.830	1.078	1.046	92.61	66.3	0.830
4.80	1.0326	1.0344	49.6	0.848	983.0	15.2	84	1.3414	2.917	1.569	0.848	1.079	1.047	92.46	67.6	0.848
4.90	1.0333	1.0351	50.6	0.866	982.7	15.6	86	1.3416	2.982	1.603	0.866	1.081	1.048	92.31	68.9	0.866
5.00	1.0340	1.0358	51.7	0.885	982.3	15.9	88	1.3418	3.046	1.638	0.885	1.083	1.049	92.15	70.1	0.885
5.20	1.0355	1.0373	53.8	0.921	981.6	16.6	91	1.3421	3.176	1.708	0.921	1.087	1.052	91.84	72.6	0.921
5.40	1.0369	1.0387	56.0	0.958	980.9	17.3	95	1.3425	3.307	1.778	0.958	1.090	1.054	91.53	75.1	0.958
5.60	1.0384	1.0402	58.1	0.995	980.2	18.0	98	1.3428	3.438	1.848	0.995	1.094	1.056	91.22	77.5	0.995
5.80	1.0398	1.0417	60.3	1.032	979.5	18.7	102	1.3432	3.570	1.919	1.032	1.098	1.058	90.90	80.0	1.032
6.00	1.0413	1.0431	62.5	1.069	978.8	19.4	105	1.3435	3.703	1.991	1.069	1.102	1.060	90.59	82.4	1.069
6.20	1.0427	1.0446	64.6	1.106	978.1	20.2	109	1.3439	3.837	2.063	1.106	1.106	1.062	90.27	84.7	1.106
6.40	1.0442	1.0460	66.8	1.144	977.4	20.9	112	1.3442	3.972	2.135	1.144	1.109	1.065	89.95	87.1	1.144
6.60	1.0456	1.0475	69.0	1.181	976.6	21.6	116	1.3446	4.107	2.208	1.181	1.113	1.067	89.63	89.4	1.181
6.80	1.0471	1.0490	71.2	1.218	975.9	22.3	119	1.3449	4.244	2.282	1.218	1.117	1.069	89.31	91.8	1.218
7.00	1.0486	1.0504	73.4	1.256	975.2	23.1	123	1.3453	4.378	2.354	1.256	1.122	1.072	88.99	94.1	1.256
7.20	1.0500	1.0519	75.6	1.294	974.4	23.8	126	1.3456	4.516	2.428	1.294	1.126	1.074	88.66	96.4	1.294
7.40	1.0515	1.0533	77.8	1.331	973.7	24.6	130	1.3460	4.655	2.503	1.331	1.130	1.077	88.33	98.7	1.331
7.60	1.0530	1.0548	80.0	1.369	972.9	25.3	133	1.3463	4.795	2.578	1.369	1.134	1.079	88.00	101.	1.369
7.80	1.0544	1.0563	82.2	1.407	972.2	26.1	137	1.3467	4.937	2.654	1.407	1.138	1.082	87.67	103.	1.407
8.00	1.0559	1.0578	84.5	1.445	971.4	26.8	140	1.3470	5.079	2.731	1.445	1.143	1.084	87.33	105.	1.445
8.20	1.0574	1.0592	86.7	1.484	970.7	27.6	144	1.3474	5.222	2.808	1.484	1.147	1.087	86.99	107.	1.484
8.40	1.0588	1.0607	88.9	1.522	969.9	28.3	147	1.3477	5.367	2.885	1.522	1.152	1.090	86.65	109.	1.522
8.60	1.0603	1.0622	91.2	1.560	969.1	29.1	151	1.3481	5.512	2.964	1.560	1.156	1.093	86.30	112.	1.560

8.80	1.0618	1.0637	93.4	1.599	968.3	29.9	154	1.3484	5.659	3.043	1.599	1.161	1.096	85.95	114.	1.599
9.00	1.0633	1.0651	95.7	1.637	967.6	30.7	158	1.3488	5.807	3.122	1.637	1.166	1.099	85.60	116.	1.637
9.20	1.0647	1.0666	98.0	1.676	966.8	31.4	161	1.3491	5.956	3.202	1.676	1.171	1.102	85.25	118.	1.676
9.40	1.0662	1.0681	100.2	1.715	966.0	32.2	165	1.3495	6.106	3.283	1.715	1.176	1.105	84.89	120.	1.715
9.60	1.0677	1.0696	102.5	1.754	965.2	33.0	168	1.3498	6.258	3.364	1.754	1.181	1.108	84.53	122.	1.754
9.80	1.0692	1.0711	104.8	1.793	964.4	33.8	172	1.3502	6.410	3.446	1.793	1.186	1.111	84.16	124.	1.793
10.00	1.0707	1.0726	107.1	1.832	963.6	34.6	175	1.3505	6.564	3.529	1.832	1.191	1.115	83.80	126.	1.832
10.50	1.0744	1.0763	112.8	1.930	961.6	36.6	184	1.3514	6.954	3.739	1.930	1.204	1.123	82.86	131.	1.930
11.00	1.0781	1.0801	118.6	2.029	959.5	38.7	193	1.3523	7.353	3.953	2.029	1.218	1.132	81.90	136.	2.029
11.50	1.0819	1.0838	124.4	2.129	957.5	40.8	202	1.3532	7.760	4.172	2.129	1.233	1.142	80.94	140.	2.129
12.00	1.0857	1.0876	130.3	2.229	955.4	42.9	211	1.3541	8.176	4.396	2.229	1.248	1.152	79.95	145	2.229
12.50	1.0894	1.0914	136.2	2.330	953.3	45.0	220	1.3549	8.602	4.625	2.330	1.264	1.162	78.96	149.	2.330
13.00	1.0932	1.0952	142.1	2.432	951.1	47.1	228	1.3558	9.038	4.859	2.432	1.280	1.173	77.97	154	2.432
13.50	1.0970	1.0990	148.1	2.534	948.9	49.3	237	1.3567	9.484	5.099	2.534	1.297	1.184	76.97	158	2.534
14.00	1.1008	1.1028	154.1	2.637	946.7	51.5	246	1.3576	9.940	5.344	2.637	1.314	1.196	75.97	163.	2.637
14.50	1.1047	1.1066	160.2	2.741	944.5	53.7	255	1.3585	10.408	5.596	2.741	1.331	1.207	74.97	167.	2.741
15.00	1.1085	1.1105	166.3	2.845	942.2	56.0	264	1.3594	10.888	5.854	2.845	1.349	1.219	73.98	171.	2.845
16.00	1.1162	1.1182	178.6	3.056	937.6	60.6	282	1.3612	11.885	6.390	3.056	1.385	1.243	72.07	179.	3.056
17.00	1.1240	1.1260	191.1	3.270	932.9	65.3	300	1.3630	12.935	6.954	3.270	1.421	1.267	70.21	166.	3.270
18.00	1.1319	1.1339	203.7	3.486	928.1	70.1	318	1.3648	14.044	7.550	3.486	1.460	1.293	68.34	193.	3.486
19.00	1.1398	1.1418	216.6	3.706	923.2	75.0	336	1.3666	15.216	8.181	3.706	1.504	1.322	66.36	199.	3.705
20.00	1.1478	1.1498	229.6	3.928	918.2	80.0	354	1.3684	16.458	8.849	3.928	1.554	1.357	64.22	204.	3.928
21.00	1.1558	1.1579	242.7	4.153	913.1	85.1	372	1.3702	17.776	9.557	4.153	1.611	1.396	61.75	209	4.153
22.00	1.1640	1.1660	256.1	4.382	907.9	90.4	391	1.3721	19.176	10.310	4.382	1.673	1.441	59.64	213.	4.382
3.00	1.1721	1.1742	269.6	4.613	902.6	95.7	409	1.3739	20.667	11.111	4.613	1.742	1.489	57.29	217	4.613
4.00	1.1804	1.1825	283.3	4.848	897.1	101.1	428	1.3757			4.848	1.817	1.542	54.93	220.	4.848
5.00	1.1887	1.1909	297.2	5.085	891.6	106.7	446	1.3776			5.085	1.898	1.600	52.58	222.	5.085
6.00	1.1972	1.1993	311.3	5.326	885.9	112.3	465	1.3795			5.326	1.986	1.662	50.26	225	5.326

LOGARITHMIC TABLES

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170						5	9	13	17	21	26	30	34	38
						0212	0253	0294	0334	0374	4	8	12	16	20	24	28	32	36
11	0414	0453	0492	0531	0569						4	8	12	16	20	23	27	31	35
						0607	0645	0682	0719	0755	4	7	11	15	18	22	26	29	33
12	0792	0828	0864	0899	0934						3	7	11	14	18	21	25	28	32
						0969	1004	1038	1072	1106	3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271						3	6	10	13	16	19	23	26	29
						1303	1335	1367	1399	1430	3	7	10	13	16	19	22	25	29
14	1461	1492	1523	1553	1584						3	6	9	12	15	19	22	25	28
						1614	1644	1673	1703	1732	3	6	9	12	14	17	20	23	26
15	1761	1790	1818	1847	1875						3	6	9	11	14	17	20	23	26
						1903	1931	1959	1987	2014	3	6	8	11	14	17	19	22	25
16	2041	2068	2095	2122	2148						3	6	8	11	14	16	19	22	24
						2175	2201	2227	2253	2279	3	5	8	10	13	16	18	21	23
17	2304	2330	2355	2380	2405						3	5	8	10	13	15	18	20	23
						2430	2455	2480	2504	2529	3	5	8	10	12	15	17	20	22
18	2553	2577	2601	2625	2648						2	5	7	9	12	14	17	19	21
						2672	2695	2718	2742	2765	2	4	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878						2	4	7	9	11	13	16	18	20
						2900	2923	2945	2967	2989	2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	123	456	789
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1 2 3	3 4 5	6 7 8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1 2 3	3 4 5	6 7 8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1 2 3	3 4 5	6 7 7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1 2 2	3 4 5	6 6 7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1 2 2	3 4 5	6 6 7
55	7404	7412	7419	7427	7435	7443	7461	7459	7466	7474	1 2 2	3 4 5	5 6 7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1 2 2	3 4 5	5 6 7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1 2 2	3 4 5	5 6 7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1 1 2	3 4 4	5 6 7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1 1 2	3 4 4	5 6 7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1 1 2	3 4 4	5 6 6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1 1 2	3 4 4	5 6 6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1 1 2	3 3 4	5 6 6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1 1 2	3 3 4	5 5 6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1 1 2	3 3 4	5 5 6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1 1 2	3 3 4	5 5 6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1 1 2	3 3 4	5 5 6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1 1 2	3 3 4	5 5 6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1 1 2	3 3 4	4 5 6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1 1 2	2 3 4	4 5 6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1 1 2	2 3 4	4 5 6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1 1 2	2 3 4	4 5 5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1 1 2	2 3 4	4 5 5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1 1 2	2 3 4	4 5 5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1 1 2	2 3 4	4 5 5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1 1 2	2 3 3	4 5 5
76	8808	8814	8820	8825	8881	8837	8842	8848	8854	8859	1 1 2	2 3 3	4 5 5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1 1 2	2 3 3	4 4 5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1 1 2	2 3 3	4 4 5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1 1 2	2 3 3	4 4 5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1 1 2	2 3 3	4 4 5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1 1 2	2 3 3	4 4 5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1 1 2	2 3 3	4 4 5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1 1 2	2 3 3	4 4 5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1 1 2	2 3 3	4 4 5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1 1 2	2 3 3	4 4 5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1 1 2	2 3 3	4 4 5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0 1 1	2 2 3	3 4 4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0 1 1	2 2 3	3 4 4
89	9494	9499	9504	9509	9515	9318	9523	9528	9533	9538	0 1 1	2 2 3	3 4 4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0 1 1	2 2 3	3 4 4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0 1 1	2 2 3	3 4 4
92	9638	9643	9647	9552	9657	9661	9666	9671	9675	9680	0 1 1	2 2 3	3 4 4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0 1 1	2 2 3	3 4 4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0 1 1	2 2 3	3 4 4
95	9777	9782	9736	9791	9795	9800	9805	9809	9814	9818	0 1 1	2 2 3	3 4 4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0 1 1	2 2 3	3 4 4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0 1 1	2 2 3	3 4 4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0 1 1	2 2 3	3 4 4
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